# EVALUATION OF BIOACCUMULATION FACTORS AND TRANSLATORS FOR METHYLMERCURY

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# AND TRANSLATORS

# FOR METHYLMERCURY

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#### **EXECUTIVE SUMMARY**

The U.S. Environmental Protection Agency (U.S. EPA) has established an ambient water quality criterion for methylmercury in fish tissue of 0.3 ppm, for the protection of human health (U.S. EPA, 2001). A criterion based on fish tissue was considered appropriate for methylmercury, in part, because fish consumption is the major route of human exposure to this contaminant (U.S. EPA, 2001). As effluent standards are necessarily water-based, and must also account for the bioaccumulation of mercury in the aquatic environment, U.S. EPA drafted a report, National Bioaccumulation Factors for Methylmercury, (U.S. EPA, 2000) describing the derivation of national bioaccumulation factors (BAFs) that can be used to convert between methylmercury tissue concentrations in various fish species and water concentrations for regulatory applications. The State Water Resources Control Board (SWRCB) funded the Office of Environmental Health Hazard Assessment to evaluate these national default bioaccumulation factors, as well as translators used to convert between different forms of mercury in water, and bioaccumulation factors derived from California data for mercury in fish and water compiled by Science Applications International Corporation (SAIC) for SWRCB into a SWRCB database.

OEHHA reviewed U.S. EPA's methods and results as presented in their report and describes their methodology, results, strengths and weaknesses of their approach, and its application to California water bodies in this report. OEHHA also reviewed the SWRCB database and BAF values, and developed alternate BAFs and translators based on California data that are analogous to those of U.S. EPA. OEHHA compared the U.S. EPA BAFs and translators to those based on California data and also tested the U.S. EPA values to determine how well they predicted fish tissue concentrations in California water bodies.

OEHHA found that U.S. EPA's methods and results met their goal of developing BAFs and translators that were broadly applicable, especially for lentic and lotic water bodies. U.S. EPA made a careful effort to compile available data and ensure quality control for the data they used. Despite their efforts, they were not able to compile data representative of all of the categories of aquatic environments and organisms. In particular, they were unable to develop BAFs for estuarine environments due to gaps in available data. U.S. EPA included some data from California in their database, but most of their data came from the Midwest United States and other areas where the source of mercury in water bodies was atmospheric deposition.

Examining data exclusively from California water bodies was an important step in evaluating whether BAFs and translators were applicable to California since the source of mercury in much of California has been legacy mercury and gold mining, and because environmental conditions in California water bodies may be different than in other areas in the U.S. EPA database. OEHHA recalculated California BAFs using the SWRCB California database. OEHHA also calculated translators for some forms of mercury using data available in this database. There were gaps in available data in the SWRCB database that prevented OEHHA from developing BAFs for some water body types (*e.g.* lentic) or trophic levels and translators for some forms of mercury in water. OEHHA developed BAFs for organisms in lotic environments and demonstrated that they

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<sup>&</sup>lt;sup>1</sup>A bioaccumulation factor is the ratio between the concentration of a chemical measured in an organism and the concentration of the same chemical in water. This ratio is derived from field-collected samples of organisms and water.

were very similar to the U.S. EPA BAFs. OEHHA also developed California estuarine BAFs for some trophic levels but there are no national values for comparison. OEHHA's estuarine values, however, were also similar to the national default values. Translators developed from the SWRCB California data were also similar to the U.S. EPA translators.

U.S. EPA developed translators and BAFs but did not test them to determine how accurately they predicted fish tissue mercury concentrations from water concentrations. OEHHA was able to test the U.S. EPA national translators and BAFs to see if they accurately predicted mercury levels in fish for several California lotic water bodies by using the SWRCB California database. OEHHA found that the national values predicted California values very well (*i.e.*, no statistical difference between measured and predicted mercury concentration) except for some water bodies where mercury concentrations in water were statistically higher. It was not possible to perform similar tests for fish in other types of water bodies because data were not available in the SWRCB database.

OEHHA has identified three alternatives for consideration by SWRCB when selecting BAFs and translators to use for California water bodies in order to implement the U.S. EPA ambient water quality criterion for methylmercury: 1) use the U.S. EPA BAFs and translators as developed by U.S. EPA; 2) use some BAF (i.e., lotic BAFs) and translator values developed from the California database, and others developed by U.S. EPA; 3) before using BAFs and translators for a methylmercury criterion, institute a program of data gathering that would supplement existing data in the SWRCB California database and enable development and testing of additional BAFs and translators using California data from different types of water bodies throughout the state. Alternative 1 is a practical solution that could be implemented without collecting additional data and would be consistent with national implementation. Based on OEHHA's evaluation using available data, it will also yield predictions that are similar to measured concentrations of mercury in fish for many, but not all, lotic water bodies. It is unknown how well this alternative will work for other California water bodies. Alternative 2 is appealing because it would incorporate California data and values for lotic water bodies, but due to gaps in the data available in the current SWRCB database it would also require using national values for lentic water bodies and some translators. However, since OEHHA's evaluation found no significant difference between U.S. EPA and California values based on the existing database, there is no scientific basis to support this alternative over Alternative 1. Alternative 3 would require collecting additional data on mercury concentrations in water and biota before full implementation and should include establishing standards for sampling, analytical methods, and Quality Assurance/Quality Control before data collection begins. Additional data collection is important to consider because OEHHA was not able to test Alternative 1 for California lentic and estuarine water bodies using the current datasets and because some water bodies were identified where Alternative 1 did not work well.

SWRCB could consider using Alternative 1 on an immediate basis while collecting additional California data for mercury concentrations in fish and water to fill gaps in available data, help identify biogeochemical factors with the greatest impact on methylmercury production and bioaccumulation, and better characterize how these factors affect variability in BAFs and translators in a longer term effort to develop better BAFs and translators for California. In

particular more fish and water data are needed to fill gaps in available data for: 1) developing lentic BAFs and translators; 2) for developing estuarine translators and BAFs for estuarine Trophic Level 3 biota; and 3) to collect enough data to test lentic and estuarine BAFs and translators. SWRCB should consider prioritizing data collection based on which type(s) of water bodies are most impacted by regulatory implementation.

Collecting data that represent a broader geological and ecological coverage of water bodies is recommended to verify, explain, and expand OEHHA's observation that the U.S. EPA BAFs did not work well for water bodies with higher mercury concentrations (approximately  $2x10^{-7}$  mg/L or more). The concentration of mercury from these water bodies was found to be more than one standard deviate from the mean for data used in testing from the SWRCB dataset. This concentration and level of variation should not be considered as screening points for outlier water bodies. Rather this observation suggests that there are water bodies and conditions in California for which the U.S. EPA BAFs and translators may not work well or be appropriate. Additional data are needed to identify these water bodies and conditions (*e.g.*, salinity or mercury source) so that the national BAFs are not applied to them and so that better translators and BAFs are developed for them.

Collecting additional California data is also recommended to better characterize variability in mercury concentration in California water bodies and biota. Natural variability in mercury concentrations will occur in water and fish from any water body. Statistical tests, such as those used by OEHHA to test BAF predictions, will account for this variability when testing for true differences among water bodies. But statistical testing is not typically used in regulatory applications and permits. One way to recognize variability in a regulatory setting would be to collect more data to separate variability due to environmental differences from variability common to all environments and use this to further verify predictions and set regulatory limits.

Further data and testing would put BAFs and translators on a more sound scientific footing in California and provide data to determine whether the mining source of much of the mercury in California water bodies (at least in the Central Valley, northern California, and the Coast Ranges) lead to significant differences in BAFs and translators for some parts of the state.

#### 1. INTRODUCTION

The U.S. Environmental Protection Agency (U.S. EPA) has established an ambient water quality criterion for methylmercury in fish tissue of 0.3 ppm, for the protection of human health (U.S. EPA, 2001). This is the first ambient water quality criterion established in tissue rather than in water. A criterion based on fish tissue was considered appropriate for methylmercury, in part, because fish consumption is the major route of human exposure to this contaminant (U.S. EPA, 2001). As effluent standards are necessarily water-based, and must also account for the bioaccumulation of mercury in the aquatic environment, U.S. EPA drafted a report, National Bioaccumulation Factors for Methylmercury, (U.S. EPA, 2000) describing the derivation of national bioaccumulation factors<sup>2</sup> (BAFs) that can be used to convert between methylmercury tissue concentrations in various fish species and water concentrations for regulatory applications. This draft report has not been finalized, but a draft implementation plan is being developed that explains a national policy to use methylmercury bioaccumulation factors in water quality regulations and permit writing (personal communication, Diane Fleck, U.S. EPA Region 9). Although the U.S. EPA report and related policies have not been adopted, the California State Water Resource Control Board (SWRCB) has begun consideration of the national bioaccumulation factors and an implementation policy to use such factors for regulation of methylmercury in ambient waters in California.

As bioaccumulation factors for different fish species may differ significantly based on environmental pH, redox potential, temperature, alkalinity, buffering capacity, suspended sediment load, and geomorphology in individual water bodies (Andren and Nriagu, 1979; Berlin, 1986; WHO, 1989), the SWRCB funded the Office of Environmental Health Hazard Assessment (OEHHA) to evaluate the derivation of national bioaccumulation factors for methylmercury and the potential for using these factors, or alternate factors based on California data, for California water bodies. OEHHA has organized this evaluation into three parts: 1) a description and critique of the national bioaccumulation factors; 2) a description and critique of California bioaccumulation factors calculated from a database of California water and tissue concentrations (referred to in this report as the SWRCB database) compiled by Science Applications International Corporation (SAIC) for SWRCB; and 3) a description and critique of a simulation in which national and California bioaccumulation factors are used to predict tissue levels from water concentrations in sample California water bodies. As part of this report, OEHHA also describes and critiques national and California translators<sup>3</sup> for mercury and methylmercury where possible.

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<sup>&</sup>lt;sup>2</sup>A bioaccumulation factor is the ratio between the concentration of a chemical measured in an organism and the concentration of the same chemical in water. This ratio is derived from field-collected samples of organisms and water

<sup>&</sup>lt;sup>3</sup> Translators are ratios between one form of a chemical and another form in the same media. In this case, the translators are for different forms of mercury in water and are based on field-collected samples.

# 2. U.S. EPA'S DEVELOPMENT OF BAFs FOR LENTIC AND LOTIC ENVIRONMENTS

U.S. EPA's BAF report (U.S. EPA, 2000) served as the primary source of information on U.S. EPA's derivation of national bioaccumulation factors and translators for OEHHA's evaluation. A brief description of the national values for BAFs and translators was also included in the final document establishing the methylmercury tissue criterion (U.S. EPA, 2001). U.S. EPA has subsequently published a final technical support document describing methods to develop bioaccumulation factors for a variety of chemicals (U.S. EPA, 2003). U.S. EPA stated that the goals for developing national methylmercury BAFs were to "represent the long-term [central tendency] bioaccumulation potential of methylmercury in aquatic biota that are commonly consumed by humans throughout the United States," and "to be applicable under as many circumstances and to as many water bodies as possible" (U.S. EPA, 2000). The national methylmercury BAFs would serve as default values that could be used when regional or other local values are not available.

U.S. EPA selected studies containing empirical field-collected data for co-located mercury or methylmercury concentrations in fish and water from a literature search and created a database that they used to calculate BAFs for aquatic organisms in Trophic Level 2, 3, and 4 (*i.e.*, the trophic levels<sup>4</sup> used to set the tissue criterion). Studies of lotic, lentic, and estuarine water bodies were included in the database. Study data had to meet certain standardized criteria for analytical chemistry data (*e.g.*, be reproducible, have a low detection limit, minimal matrix interferences, and use appropriate analytical techniques) to be included in the database. In most cases, methylmercury results collected prior to 1990 were not used because they did not meet these criteria. A cutoff was set for the literature review and studies published after April 1999 were not included in the literature search or resulting database. The database itself was not available for OEHHA to review, so it was not possible to determine exactly which data were used by U.S. EPA, or to carry out calculations using the raw database data. Instead, it was necessary to use the summary information in the draft U.S. EPA document (U.S. EPA, 2000) to describe the U.S. EPA data and carry out comparative calculations.

U.S. EPA used methodology from the Ambient Water Quality Criteria Derivation Methodology Human Health Technical Support Document, Final Draft (U.S. EPA, 1998) and the Mercury Study Report to Congress (U.S. EPA, 1997a) to derive their national BAF and translator values. Fish were assigned to trophic levels based on U.S. EPA guidance (U.S. EPA, 1995) and information from the selected studies. There were some exceptions to these methods and guidelines. In some cases, zooplankton, which are not consumed by humans, were used to calculate Trophic Level 2 BAFs. And in other cases, mercury concentration data in Trophic Level 3 and 4 fish were based on whole body data or tissue samples not clearly identified as

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<sup>&</sup>lt;sup>4</sup> Trophic means eating. Trophic levels are steps in a food chain characterized by feeding interactions. Energy moves up the food chain from lower to higher trophic levels as a result of organisms in one level feeding on those in a lower level. Organisms in Trophic Level 1 are primary producers that fix energy in an ecosystem (*e.g.*, plants and other organisms that fix energy. Trophic Level 2 organisms are herbivorous and feed on the primary producers. In aquatic ecosystems Trophic Level 3 organisms eat the herbivores and are forage fish for the next level. Trophic Level 4 organisms are carnivorous and eat primarily Trophic Level 3 organisms. In aquatic ecosystems these are the top predatory fish. Humans mostly eat fish and other aquatic organisms from Trophic Level 3 and 4.

fillet, muscle, whole body, or other tissue types. U.S. EPA attempted to treat all samples equally when deriving trophic level BAFs by first calculating individual mean BAFs for species in Trophic Level 3 and 4 within studies and then calculating a mean for all species in the same trophic level. This was not always possible for Trophic Level 2 because zooplankton collections contain a mix of species. It is not possible to describe the treatment of data and samples in detail without the full database and associated information. U.S. EPA expressed both species and trophic level BAFs as unweighted geometric means. The U.S. EPA BAF report does not discuss statistical testing of the distributions of individual studies or the database data at the species or trophic level, but states that geometric means were used primarily because the factors underlying BAF variability were believed to be multiplicative rather than additive, and also in part for convenience (U.S. EPA, 2000).

U.S. EPA derived BAFs using the ratio of methylmercury in field-collected data from biota and water as shown in Equation 1. Mercury in biota was most often measured and reported as total mercury (which can include inorganic and methylmercury). When only total mercury was reported in studies, U.S. EPA made assumptions about the percent of total mercury that was methylmercury for organisms at Trophic Levels 2, 3, and 4 in different environments. Equation 1 is a simple empirical model estimating the magnitude of accumulation of methylmercury from water into biota (*e.g.*, zooplankton and fish). BAFs calculated using this equation only require two parameters (a tissue concentration and a water concentration) and have units of L/kg because generally mercury concentrations in water are reported in mg/L and concentrations in biota are reported in mg/kg (wet weight). More complex mechanistic models that use multiple parameters to model individual steps in methylmercury production, uptake, and accumulation have also been used to estimate the relationship between methylmercury in water and biota (Hope, 2003; Kamman, *et al.*, 2003). More complex models would require a great deal more data than was available in most studies in the U.S. EPA database.

#### Equation 1.

$$BAF\,,\,L/kg \quad = \quad \frac{mercury\,\,in\,\,biota\,,\,mg/kg}{dissolved\,\,methylmercury\,\,in\,\,water\,,\,mg/L}$$

Using Equation 1 and data in their database, U.S. EPA calculated BAFs for organisms in lentic (*e.g.*, lakes) and lotic (*e.g.*, rivers) water bodies for the trophic levels used to establish the ambient water criterion (Trophic Levels 2, 3, and 4) for methylmercury (U.S. EPA, 2001). U.S. EPA chose to combine the BAFs at the same trophic level for lentic and lotic water bodies into one national BAF for each trophic level. U.S. EPA did not derive BAFs for the estuarine environment because of insufficient data.

U.S. EPA suggests that the national BAFs are functional default values that can be used when more representative regional, local or site-specific BAFs are not available (U.S. EPA, 2003). BAFs can be used to solve for the numerator or denominator in the above equation when the other is known, *i.e.*, by using the appropriate BAF, a concentration of methylmercury in biota can be calculated from known dissolved methylmercury concentrations in water, or a water

concentration of dissolved methylmercury can be calculated from known biota methylmercury concentrations.

U.S. EPA also used data from their database to calculate national translator values to convert between various forms of mercury in water (e.g., between total mercury and dissolved methylmercury). Their translator values were calculated as simple ratios between one mercury form and another. U.S EPA calculated separate geometric mean national translators for lentic and lotic environments (U.S. EPA, 2000). U.S. EPA did not discuss why they did not combine translators as they had done for national BAFs. Translators were essential to the U.S. EPA's derivation of BAFs because many measurements of water mercury concentrations in studies included in the U.S. EPA database were for a form other than dissolved methylmercury. Initially, U.S. EPA calculated BAFs based on studies that had directly measured dissolved methylmercury in water; these were "directly estimated" BAFs. U.S. EPA then used the national translators to convert water measurements from other studies into dissolved methylmercury to calculate additional BAFs. These were termed "converted" BAFs, and using them increased the number of studies and data in the U.S. EPA database. U.S. EPA combined directly estimated and converted BAFs to derive the national values. U.S. EPA's derivation of the national BAFs for Trophic Levels 2, 3, and 4 is discussed in more detail below. U.S. EPA did not develop BAFs for Trophic Level 1 as these primary consumers are not normally eaten by humans.

Directly estimated BAFs for lentic or lotic environments are those from studies where dissolved methylmercury was measured in water and then used in the calculation of the BAF. U.S. EPA defined the directly estimated BAF for each trophic level as the average methylmercury concentration (often measure as total mercury) accumulated by all possible routes of exposure in organisms of that trophic level, divided by the average directly measured dissolved methylmercury concentration in water.

Converted BAFs for lentic or lotic environments, on the other hand, were defined as the average methylmercury concentration in each trophic level (often measured as total mercury) accumulated by all possible routes of exposure, divided by the dissolved methylmercury concentration in water obtained from conversion of measured total mercury to dissolved methylmercury using the appropriate translator determined from other studies.

#### 2.1 U.S. EPA BAFS FOR LENTIC ENVIRONMENTS

#### 2.1.1 Directly Estimated Trophic Level 2 BAFs, Lentic Environments

The BAFs for zooplankton in lentic environments for Trophic Level 2 are listed in Table 3-1 in the National Bioaccumulation Factors for Methylmercury (U.S. EPA, 2000). Two studies were used to develop the BAFs: one, which evaluated 15 lakes in Wisconsin (Watras *et al.*, 1998), and another, which surveyed 12 lakes in northeast Minnesota (Monson and Brezonick, 1998). As noted above, total mercury, rather than methylmercury, was measured in zooplankton and Trophic Level 2 organisms in many studies. In order to calculate BAFs for these and other studies in their database, U.S. EPA assumed that 44 percent of the measured total mercury in biota in lentic environments for this trophic level was methylmercury. U.S. EPA calculated

geometric mean BAF values for the Wisconsin and Minnesota studies of 42,400 L/kg and 172, 764 L/kg, respectively, and a combined geometric mean BAF of 85,600 L/kg.

### 2.1.2 Directly Estimated Trophic Level 3 BAFs, Lentic Environments

The U.S. EPA assumed that 100 percent of the mercury measured as total mercury in this trophic level was methylmercury. BAFs for this trophic level (forage fish) were developed from five studies and are listed in Table 3-2 in the National Bioaccumulation Factors for Methylmercury (U.S. EPA, 2000). U.S. EPA derived a combined BAF of 504,000 L/kg for shiner and yellow perch in 15 Wisconsin lakes using data from Watras et al., (1998). Using data from Becker and Bigham (1995), U.S. EPA derived a BAF of 666,666 L/kg for gizzard shad from Lake Onondaga, New York. A BAF of 1,460,000 L/kg for yellow perch at Lake Iso Valkjarvi, Finland, was generated from Rask and Verta (1995), while a combined BAF of 1,530,000 L/kg was established for silversides and juvenile bass in Clear Lake, California, using data from Suchanek et al. (1993). The Suchanek data include silversides, a fish not usually consumed by humans. It is, nevertheless, a species that probably falls in this trophic level. Finally, U.S. EPA used data from Mason and Sullivan (1997) to develop a BAF of 4,170,000 L/kg for bloater in Lake Michigan. The geometric mean BAF values for these five studies ranged from 504,000 L/kg to 4,170,000 L/kg, a difference of less than 10-fold despite the wide geographic distribution of these studies (United States and Finland). The overall combined geometric mean BAF determined by U.S. EPA for this trophic level was 1,260,000 L/kg.

# 2.1.3 Directly Estimated Trophic Level 4 BAFs, Lentic Environments

Fish in Trophic Level 4 are predatory and feed predominantly on other fish. U.S. EPA assumed that the measured total mercury in these species was 100 percent methylmercury. Four North American studies were used in the BAF calculations; results are summarized in Table 3-3 in the National Bioaccumulation Factors for Methylmercury (U.S. EPA, 2000). U.S. EPA derived a combined BAF of 4,000,000 L/kg for smallmouth bass and walleye from Lake Onondaga, New York based on data in Becker and Bigham (1995), and an overall BAF of 5,860,000 L/kg for northern pike and walleye in four lakes in Manitoba, Canada, studied by Jackson (1991). Using data from Suchanek, *et al.*, (1993) from Clear Lake, California, U.S. EPA derived a BAF of 8,060,000 L/kg for largemouth bass. And finally, U.S. EPA used data from Mason and Sullivan (1997) to derive a BAF of 11,400,000 L/kg for lake trout from Lake Michigan. The BAFs for these studies ranged from 4,000,000 L/kg to 11,400,000 L/kg, a difference of less than three-fold. The geometric mean BAF for these studies was 6,800,000 L/kg.

# 2.1.4 Converted Trophic Level 2 BAFs, Lentic Environments

When mercury was measured as total mercury, U.S. EPA assumed that 44 percent was methylmercury for this trophic level. Five studies, all from North America, were used in these BAF calculations. The study results are summarized in Table 5-4 in the National Bioaccumulation Factors for Methylmercury (U.S. EPA, 2000). U.S. EPA derived an aggregate BAF of 61,757 L/kg, for zooplankton from 15 Wisconsin lakes using data from Watras *et al*, (1998). A BAF of 104,405 L/kg for zooplankton collected on an 80 µm filter in several lakes in the Experimental Lakes Region in NW Ontario, Canada, was derived from Paterson *et al*. (1998). A second BAF of 283,850 L/kg for zooplankton collected on a 400 µm filter was also derived

from Paterson *et al.*, (1998). An aggregate BAF for zooplankton (filter size >300 μm) from 12 lakes in Minnesota of 127,000 L/kg was developed from Monson and Brezonick (1998); a second BAF of 326,264 L/kg for plankton (filter size 1 not reported) from Tamarack Lake, Minnesota, was derived from data from the same study. The BAFs from these studies ranged from 61,757 to 326,264 L/kg, a difference of slightly more than six-fold. The unweighted BAF geometric mean for these studies was 149,960 L/kg.

# 2.1.5 Converted Trophic Level 3 BAFs, Lentic Environments

U.S. EPA assumed that measured total mercury was 100 percent methylmercury for this trophic level. Data from the four studies used to derive BAFs for this trophic level are summarized in Table 5-5 in the National Bioaccumulation Factors for Methylmercury (U.S. EPA, 2000). All studies were from the Midwestern United States. An aggregate BAF of 734,095 L/kg for shiner and yellow perch from 15 Wisconsin lakes was derived from Watras et al. (1998). Data from Glass et al. (1992) were used to derive a BAF of 1,022,326 L/kg for yellow perch from Sand Point Lake, Minnesota, and a BAF of 1,297,052 L/kg for yellow perch from Crane Lake, Minnesota. Finally, a BAF of 3,262,643 L/kg was derived for young-of-the-year bluegill (i.e., fish in the same age cohort that were less than one year old) at Tamarack Lake, Minnesota, based on data from Monson and Brezonick, (1998). These immature bluegill had the highest BAF in the reported studies, although they are too small for human consumption. BAFs in this age class of fish might reflect high intake prior to subsequent growth dilution. Some unknown amount of variation will be introduced when studies using fish of different ages and sizes are combined because mercury levels in fish are known to vary with age and size (Wiener, et al., 2003). The geometric mean BAF value for these studies was 1,330,000 L/kg, with values ranging from 734,095 to 3,262,643 L/kg. This less than five-fold range, while still broad, is smaller than the approximately 10-fold range for directly measured BAFs in Trophic Level 3 fish. The closer geographic proximity of these studies and similarities in species used to derive BAFs might account, in part, for the tighter range. However, the results also show that there remains a broad range in BAFs from different lakes even when the lakes are from a more restricted geographic area.

### 2.1.6 Converted Trophic Level 4 BAFs, Lentic Environments

U.S. EPA assumed that 100 percent of measured total mercury was methylmercury for this trophic level. BAF values from two studies are summarized in Table 5-6 in the National Bioaccumulation Factors for Methylmercury (U.S. EPA, 2000). A BAF of 3,954,284 L/kg for walleye from various unspecified Lakes in Minnesota was derived from Glass *et al.* (1999), and a BAF of 4,203,000 L/kg was derived for pike from the same study. The geometric mean for these data was 4,100,000 L/kg.

<sup>&</sup>lt;sup>1</sup> The US EPA did not regularly report filter sizes for each study. When they were reported, they are noted. Different size filters will capture different sizes and kinds of planktonic organisms. This introduces an unknown amount of variability in BAFs for this trophic level.

#### 2.1.7 Combined Direct and Converted BAFs, Lentic Environments

The U.S. EPA combined the direct and converted BAFs for Trophic Levels 2, 3, and 4 for lentic ecosystems to obtain the values presented in Table 1 of this report. U.S. EPA stated that it was justified to combine the direct and converted data into a composite value because, when graphically displayed, the data appeared to be in the same range. U.S. EPA did not statistically test for differences in the means between direct and converted BAFs for each trophic level. Statistical testing may have been limited by the available small dataset.

The differences between the geometric mean direct and converted BAFs in Trophic Levels 2, 3, and 4 were less than two-fold for each trophic level. For Trophic Levels 2 and 3, the converted BAF is higher than the directly measured BAF. For Trophic Level 4, the directly measured BAF was higher than the converted BAF. The combined geometric mean for direct and converted BAFs shows that the BAF for Trophic Level 3 is about 10-fold greater than that for Trophic Level 2 (1,115,000 vs. 127,000 L/kg), and the BAF for Trophic Level 4 is about five-fold greater than the BAF for Trophic Level 3 (5,740,000 vs. 1,115,000 L/kg).

**Table 1.** Direct and converted Bioaccumulation Factors (L/kg) for trophic levels in the lentic environment\*

Trophic level	2		3	3	4	
BAF	<u>Direct</u>	Converted	Direct	Converted	Direct	Converted
GM <sup>1/</sup> Combined	85,600	150,000	1,260,000	1,330,000	6,800,000	4,080,000
GM <sup>2/</sup>	127,8	800	1,115	5,000	5,740	,000

<sup>1</sup> GM: Geometric Mean

#### 2.2 U.S. EPA BAFS FOR LOTIC ENVIRONMENTS

# 2.2.1 Directly Estimated Trophic Level 2 BAFs, Lotic Environments

U.S. EPA assumed that 49 percent of the total mercury measured in organisms in lotic environments at this trophic level was methylmercury. U.S. EPA used data from three studies to derive these BAFs. Data from a study in the North Florida Everglades reported by Cleckner *et al.*, (1998) for whole body fish samples from three species (*Gambusia sp.*, *Heterandia formosa*, and *Lucanian goodie*) were combined to obtain a BAF of 34,474 L/kg. Another study by Miles and Fink, (1998), also in the North Florida Everglades, was used to derive a BAF of 271,831 L/kg. Finally, a BAF of 608,728 L/kg for stonerollers, which are zooplankton, was derived from a study in East Popular Creek, Tennessee (Hill *et al.*, 1996). The unweighted geometric mean for these studies was 178,678 L/kg. Since only three studies met U.S. EPA's criteria, fish and zooplankton were used for derivation of the BAF for this trophic level. These data are listed in Table 5-7 of the National Bioaccumulation Factors for Methylmercury U.S. EPA, (2000).

<sup>2</sup> Geometric Mean (GM) after combining direct and converted BAFs for the lentic environment

<sup>\*</sup>Summarized from Tables 5-12, 5-14 (U.S. EPA, 2000)

# 2.2.2 Directly Estimated Trophic Level 3 BAFs, Lotic Environments

U.S. EPA assumed that 100 percent of the measured total mercury was methylmercury for this trophic level (forage fish). Studies by Lores *et al.* (1998) in South Florida canals provided data for the following BAFs: spotted tilapia: 334,325 L/kg; bluegill: 1,286,156 L/kg; and spotted sunfish: 1,472,669 L/kg. Data for bluegills from a study in the North Florida Everglades (Miles and Fink, 1998) yielded a BAF of 577,465 L/kg. Data from studies on creeks in Tennessee yielded a BAF of 2,026,609 for shiner (Hill *et al.*, 1996) and 4,863,263 L/kg for redbreast (DOE, 1997). A second BAF for redbreast of 11,250,000 L/kg was also derived (DOE, 1997). The geometric mean for these data was 1,636, 298 L/Kg, with a substantial range of about 34-fold. These data are presented in Table 4-2 in the National Bioaccumulation Factors for Methylmercury U.S. EPA, (2000).

#### 2.2.3 Directly Estimated Trophic Level 4 BAFs, Lotic Environments

U.S. EPA assumed that 100 percent of the measured total mercury was methylmercury for this trophic level (piscivorous fish). Two studies were used to estimate the BAF for this trophic level. One study of largemouth bass in the Florida Everglades yielded a BAF of 985,915 L/kg (Miles and Fink, 1998). Another study of largemouth bass in some South Florida Canals yielded a BAF of 6,464,028 L/kg (Lores *et al.*, 1998). The geometric mean for these data is 2,524,477 L/kg. These data are presented in Table 4-3 in the National Bioaccumulation Factors for Methylmercury U.S. EPA, (2000).

# 2.2.4 Converted Trophic Level 2 BAFs, Lotic Environments

U.S. EPA assumed that 49 percent of the measured total mercury was methylmercury for this trophic level. U.S. EPA used three studies to derive the BAF for this trophic level. Data from a study in the Tom River in Siberia (Papina, *et al.*, 1995) yielded a BAF of 8,661 L/kg for zooplankton. Data from Stober *et al.* (1995) yielded a BAF of 105,128 L/kg for mosquitofish in South Florida Everglade canals. Finally, data from Miles and Fink, (1998) from the north Florida Everglades yielded a BAF of 260,811 L/kg, also for mosquito fish. The unweighted geometric mean for these data was 62,000 L/kg, with a nearly 30-fold difference in converted BAF values for this trophic level. Data are listed in Table 5-8 in the National Bioaccumulation Factors for Methylmercury U.S. EPA, (2000). The small number of studies available and wide geographic range may have contributed to the difference in the BAFs between the studies.

# 2.2.5 Converted Trophic Level 3 BAFs, Lotic Environments

U.S. EPA assumed that 100 percent of the measured total mercury was methylmercury for this trophic level. Acceptable data from seventeen studies were used from various geographic regions for this BAF. Six studies in the Tom River in Siberia, Papina *et al.*, (1995) yielded the following BAFs for six different species: grayling: 35,238 L/kg; carp: 52,857 L/kg; roach: 70,476 L/kg; perch: 79,286 L/kg; dace: 132,143 L/kg; and bream: 211,429 L/kg. Data from Glass *et al.* (1992), for St. Louis River in Minnesota yielded the following BAFs for five different species: yellow perch: 345,622 L/kg; Johnny darter: 391,705 L/kg: log perch: 460,829 L/kg; spottail shiner: 691,244 L/kg; and emerald shiner: 921,659 L/kg. Studies in South Florida Canals by Lores *et al.* (1998) yielded data to derive BAFs for spotted sunfish (524,381 L/kg),

bluegill (933,810 L/kg), spotted tilapia (1,132,656 L/kg), and mayan cichlid (1,326,049 L/kg). Data from Miles and Fink (1998) were used to derive a BAF for bluegill in the North Florida everglades of 1,130,723 L/kg. Lastly, a BAF of 1,499,688 L/kg for a perch/roach mix from the Kokenmaenjoki River Estuary, Finland, was derived from Schultz *et al.* (1995). This data set is the largest of all those used for either direct or converted estimation of BAF values and the data were listed in Table 5-9 in the National Bioaccumulation Factors for Methylmercury U.S. EPA, (2000). Although additional data might yield a more representative overall BAF, the studies do include the broadest geographic distribution of water bodies of any trophic level category. BAFs range more than 40-fold from the grayling (35,238 L/kg) in the Tom River in Siberia to 1,499,688 L/kg for the perch/roach found in the Kokenmaenjoki River Estuary, Finland. The broad geographic distribution and related environmental differences may contribute to this wide range. The geometric mean for these data is 346,613 L/kg.

### 2.2.6 Converted Trophic Level 4 BAFs, Lotic Environments

U.S. EPA assumed that 100 percent of the measured total mercury was methylmercury for this trophic level. Data from studies in the Tom River, Siberia (Papina *et al.*, 1995) yielded BAF values for burbot and pike of 96,905 and 352,381 L/kg, respectively. A BAF for bass from North Florida Everglades of 1,930,502 L/kg was derived based on data in Miles and Fink (1998), while a BAF value of 7,308,573 L/kg for pike from the Kokenmaenjoki River Estuary, Finland, was derived from the data of Schultz *et al.* (1995). Finally, a BAF of 10,401,681 L/kg for largemouth bass was derived from Lores *et al.*, (1998). The unweighted geometric mean for these data was 1,380,361 L/kg, and the data were listed in Table 5-10 in the National Bioaccumulation Factors for Methylmercury U.S. EPA, (2000).

#### 2.3 COMBINED DIRECT AND CONVERTED BAFS FOR LOTIC ENVIRONMENTS

The U.S. EPA combined the direct and converted data for BAFs for Trophic Levels 2, 3 and 4, respectively, in lotic ecosystems to obtain the values presented in Table 2 in this report. The rationale expressed by the U.S. EPA for the combination of the direct and converted data into a composite value for this ecosystem is that the data, when graphically displayed, appeared to be in the same range. When the direct and converted BAFs are compared for these trophic levels, all converted values are less than directly measured values with the differences ranging from about two- to four-fold. For example, the direct and converted BAFs for Trophic Level 2 are 179,000 and 61,900 L/kg, respectively, a difference of slightly less than three-fold. The combination of the direct and converted BAFs for Trophic Level 2, 3, and 4 are 105,000, 517,000 and 1,240,000 L/kg, respectively.

**Table 2.** Direct and converted Bioaccumulation Factors (L/kg) for trophic levels in the lotic environment\*

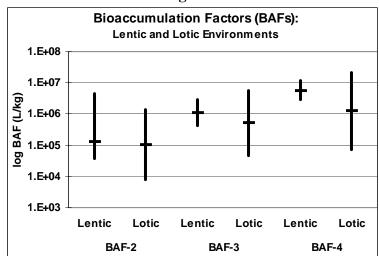
Trophic level	2		3	3	4	
BAF	Direct	Converted	<u>Direct</u>	Converted	<u>Direct</u>	Converted
GM <sup>1/</sup> Combined	179,000	61,900	1,640,000	346,000	2,520,000	1,380,000
GM <sup>2/</sup>	105,0	000	517,	000	1,240	,000

<sup>1</sup> GM: Geometric Mean

# 2.4 COMBINATION OF LENTIC AND LOTIC BAFS TO DERIVE NATIONAL BIOACCUMULATION FACTORS

The U.S. EPA, after examining the data for the combined lentic and lotic BAFs at each trophic level, decided that it was appropriate to combine lentic and lotic BAFs. The primary reason given by the U.S. EPA for combining BAFs for lentic and lotic environments was that there was no difference between these BAFs when tested statistically (p >0.05). Figure 1 shows the overlap at the lower and upper bounds (5<sup>th</sup> and 95<sup>th</sup> percentiles) of the distributions of lentic and lotic BAFs at each trophic level for the U.S. EPA geometric mean BAFs.

Figure 1



BAF-2, BAF 3, and BAF-4 are for Trophic Level 2, 3, and 4 biota, respectively. The mean values used to construct this figure above are from U.S. EPA (2000) as shown in the Table 3.

The horizontal bar is the geometric mean. Vertical bar is the 5<sup>th</sup> to 95<sup>th</sup> percentile.

<sup>2</sup> Geometric Mean (GM) after combining direct and converted BAFs for the lotic environment

<sup>\*</sup> Summarized from Tables 5-13 and 5-14 (U.S. EPA, 2000)

**Table 3**. National Bioaccumulation Factors (L/kg) for fish in Trophic Levels 2, 3 and 4

-	2	2	3		4	
BAF	<u>Lentic</u>	<u>Lotic</u>	<u>Lentic</u>	<u>Lotic</u>	<u>Lentic</u>	<u>Lotic</u>
GM <sup>1/</sup> Combined GM <sup>2/</sup>	127,800 117,	105,000 000	1,115,000 680,0	517,000	5,740,000 2,670,	1,240,000 000

- 1 GM: Geometric Mean for each environment
- 2 Geometric Mean (GM) after combining lentic and lotic BAFs for both environment

Figure 2 diagrams the process that U.S. EPA utilized to derive the national BAFs for Trophic Levels 2, 3 and 4. The national BAFs are applicable to both lotic and lentic aquatic environments (U.S. EPA, 2000). U.S. EPA did not develop estuarine BAFs because their data set contained insufficient data of adequate quality.

National Bioaccumulation Factors (BAFs)

US EPA Method

Lentic\*

Direct + Converted

Lotic\*

Lotic\*

Lotic\*

Lotic\*

Lotic\*

Lotic\*

National BAFs\*

\*Trophic levels 2-4

Figure 2

#### 2.5 U.S. EPA's DEVELOPMENT OF TRANSLATORS

Mercury, like other metals in water, can occur in a number of physical and chemical forms. Physically, mercury can be freely dissolved or bound to organic matter or particles suspended in water. And chemically, mercury can be found as elemental mercury, inorganic ionic mercury, or organic mercury (*e.g.*, methylmercury or dimethylmercury). Thus, mercury in water can be separately characterized physically (*e.g.*, total suspended mercury including all chemical forms) or chemically (total methylmercury including all physical forms). In most cases "total mercury" refers to a measured total concentration of all physical and chemical forms in water. U.S. EPA determined that dissolved methylmercury was the most relevant form of mercury for bioaccumulation and calculating BAFs (U.S. EPA, 2000 and 2003). But dissolved methylmercury was not always the form measured in the studies U.S. EPA identified for

inclusion in their database. Hence, translators were necessary to convert between other forms of mercury measured in water and dissolved methylmercury for BAF calculations. In addition, U.S. EPA intends to use translators for similar conversions for regulatory purposes to "convert the dissolved criteria back to a total metal concentration for use in the waste limit calculations. The translator is the fraction of the total recoverable metal in the downstream water that is dissolved,  $f_d$ . The translator is used to estimate the concentration of the total recoverable metal in the effluent discharge that equates to the criterion concentration [methylmercury] in the receiving water body."

U.S. EPA used a general equation for calculating fractional translators ( $f_d$  s) for metals. This is the ratio between the total measurable concentration ( $C_t$ ) of a metal in water and the dissolved concentration ( $C_d$ ) of the metal in water:  $f_d = C_d/C_t$ . U.S. EPA was most interested in translators that would yield the dissolved fraction of methylmercury ( $f_{dmHg}$ ). These translators would always be based on a measured concentration of dissolved methylmercury ( $C_{dmHg}$ ) and either a total concentration in water based on measured total mercury ( $C_{thg}$ ) or measured total methylmercury ( $C_{tmHg}$ ). The best way to estimate dissolved mercury forms (either methylmercury or inorganic) is by passing the water through filters with micron-sized pores and collecting the water and the filter. The dissolved concentration of one or more mercury species is measured in the water that passes through the filter. The total concentration of the same species is the sum of the concentrations of those species measured on the filter and those in the water that passes through.

U.S. EPA used measured values for  $C_d$  and  $C_t$  determined for the mercury species of interest from studies in their database. They used data criteria to select studies for the development of translators that were similar to the data requirements for the development of BAFs. Briefly, the studies must use clean techniques, have adequate Quality Assurance/Quality Control (QA/QC) and the methods must have a detection limit that unambiguously allows the quantitation of low  $(10^{-7} \text{ to } 10^{-9} \text{ mg/L})$  concentration of species such as dissolved methylmercury. The low detection requirement is especially critical for dissolved methylmercury, which may be less than 10 percent of total mercury (*i.e.*, the concentration of all physical and chemical forms) in an aquatic environment.

U.S. EPA calculated the geometric mean of the ratio,  $f_d = C_d/C_t$  for several measurements in several water bodies as a measure of central tendency for deriving national translators. U.S. EPA did not specifically discuss the rationale for the selection of a geometric mean over an arithmetic mean for the estimate of mercury  $f_ds$  (translators). Using geometric means for translators was consistent with their approach for BAFs. U.S. EPA developed translators for the lentic and lotic environments but did not combine them as they did for BAFs.

The following discussion summarizes the studies that U.S. EPA utilized to derive water translators for lentic and lotic aquatic systems.

<sup>&</sup>lt;sup>5</sup> Section II: Default chemical translator for mercury and methylmercury., (U.S. EPA 2000), p2

# 2.5.1 Translator For Conversion Of Total Mercury To Dissolved Methylmercury (MeHg<sub>d</sub>/Hg<sub>t</sub>), Lentic Environments

U.S. EPA used nine studies to derive a translator representing the fractional relationship between dissolved methylmercury and total mercury in water. Table 4 lists the studies and is based on the data in Table 2 in Appendix B of the National Bioaccumulation Factors for Methylmercury (U.S. EPA, 2000). Geographically, the studies were widely distributed: two were from Europe (France and Finland); the rest were from the United States, including one in California at Clear Lake, California. The data range was about 70-fold (0.002 - 0.139). The geometric mean was 0.032. This indicates that dissolved methylmercury was about 3.2 percent of total mercury, *i.e.*, physical and chemical mercury, in these water bodies.

**Table 4.** Lentic Environments: Dissolved methylmercury as a fraction of total mercury  $(MeHg_d/Hg_t)$ 

MeHg <sub>d</sub> /Hg <sub>t</sub> *	Location	Comments	Author
0.002	Clearlake, CA	Only CA study	Suchanek et al., 1998
0.014	Pavin Lake, France	Epilimnion @ 30-40 M	Cossa and Martin, 1991
0.020	Vandercook Lake, WI	-	Watras et al., 1994
0.031	Lake Michigan	-	Mason and Sullivan, 1997
0.044	Little Rock Lake, WI	-	Watras et al., 1994
0.061	Pallette Lake WI	-	Watras et al., 1994
0.067	Lake Iva, Finland	-	Verta and Matilainen, 1995
0.078	North Wisconsin Lakes	15-lake composite	Watras et al., 1998
0.139	Max Lake, WI	-	Watras et al., 1994
Geometric Mean	n = 0.032		
* Dissolve forms)	d methylmercury/Total mercury	(all physical and chemical	

# 2.5.2 Translator For Conversion Of Total Mercury To Dissolved Methylmercury (MeHgd/Hgt), Lotic Environments

U.S. EPA selected 13 studies for the derivation of the translator for conversion between dissolved methylmercury and total mercury in lotic environments. Table 5 lists the studies utilized by the U.S. EPA. These data were taken from Table 7 in Appendix B of the National Bioaccumulation Factors for Methylmercury U.S. EPA (2000). There were no acceptable studies in the U.S. EPA database for this translator using data from California water bodies. The closest geographically to California was the study by Bonzongo *et al.*, (1998) from the Carson River, Nevada. Two studies were for water bodies outside of the U.S. The translator values ranged from 0.002 to 0.051, or about 25-fold. The geometric mean for these data is 0.014, which means that 1.4 percent of total mercury (all physical and chemical forms) in these lotic systems is dissolved methylmercury.

Comparison of the lentic and lotic translators for dissolved methylmercury and total mercury in water suggests that there is more dissolved methylmercury in lentic than lotic water bodies. U.S. EPA speculated that the higher titer of organic matter in lentic systems compared to lotic environments may play some role in increasing dissolved methylmercury in lentic systems. U.S. EPA did not discuss whether they considered combining the translators for the two environments as they had done for the BAFs. OEHHA compared the data sets for the lentic and lotic environments using a two-tail t-test assuming unequal variance and calculated a statistical value of p = 0.06, which is just over a standard level of statistical significance (p < 0.05). This is not a clear reason to combine or separate lentic and lotic translators.

**Table 5**. Lotic Environments: Dissolved methylmercury as a fraction of total mercury

MeHg <sub>d</sub> /Hg <sub>t</sub> *	Location	Comments	Author
0.002	For Divor WI		Hughan et al. 1009
	Fox River, WI	-	Hurley <i>et al.</i> , 1998
$0.002^{+}$	Anacostia River, MD	High flow	Mason and Sullivan, 1998
0.007	Hinds Creek, TN	-	D.O.E., 1997
$0.010^{+}$	Anacostia River, MD	-	Mason and Sullivan, 1998
0.012	Poplar Creek, VT	-	Campbell et al., 1998
0.013	Grand River MI	-	Hurley et al., 1998
$0.017^{\bullet}$	Patuxent, MD	-	Benoit, 1998
0.017	Sheboygan River, WI	-	Hurley et al., 1998
0.018	Wisconsin Rivers	Composite of 39	Hurley et al., 1995
0.034	Wisconsin Rivers	Composite of 7	Babiarz et al., 1998
0.038	Carson River, NV	- -	Bonzongo et al., 1996
0.041	Pere Marquette River, MI	-	Hurley et al., 1998
0.051	Manistique River, MI	-	Hurley et al., 1998
Geometric Me	an = 0.014		
* Dissolved	methylmercury/Total mercury		
+ 0.8 um filt			
• 0.2 um filt	er		

# 2.5.3 Translator For Conversion Of Total Methylmercury To Dissolved Methylmercury (MeHgd/Hgt), Lentic Environments

The 13 studies U.S. EPA used to derive the translator for lentic environments are listed in Table 6. They were taken from Table 3 in the National Bioaccumulation Factors for Methylmercury (U.S. EPA, 2000). The translator values for water bodies in the table range from 0.303 to 1.02 with an unweighted geometric mean value of 0.613. This is only about a three-fold difference between values even though several water bodies were in Europe. Data from two studies conducted at Clear Lake, California are included. One study in the upper arm of Clear Lake found that the dissolved methylmercury was about 43 percent of the total methylmercury, while the other study observed that dissolved methylmercury and total mercury were nearly equivalent (*i.e.* dissolved methylmercury was 102 percent of total mercury), a difference of about two-fold. The high value might be related to conditions at Clear Lake associated with drainage from a

mercury mine. While mine drainage (from either mercury or gold mining using mercury) may be unusual source of mercury in most states it is a common source in California. These data show that, in some lakes, dissolved methylmercury in water can be nearly equivalent to total methylmercury.

**Table 6.** Lentic Environments: Dissolved methylmercury as a fraction of total methylmercury (MeHg<sub>d</sub>/MeHg<sub>t</sub>)

MeHg <sub>d</sub> /MeHg <sub>t</sub> *	Location	Comments	Author
0.303	Vandercook Lake, WI	-	Bloom et al., 1991
0.353	Onondoga Lake, NY	-	Henry et al., 1995
0.425	Clear Lake, CA	Upper arm	Suchanek et al., 1998
0.577	Pallete Lake, WI	-	Bloom et al., 1991
0.600	Lake Hako, Finland	-	Verta and Matilainen, 1995
0.645	Pavin Lake, France	Epilimnion @ 30-40 m	Cossa et al., 1994
0.667	Little Rock Lake, WI	<del>-</del>	Bloom et al., 1991
0.698	Wisconsin Lakes	15-lake composite	Watras et al., 1998
0.72	Max Lake, WI	-	Bloom et al., 1991
0.762	Lake Michigan, MI	-	Mason and Sullivan, 1997
0.79	Lake Iva, Finland		Verta and Matilainen, 1995
0.82	Lake Keha, Finland		Verta and Matilainen, 1995
1.02	Clear Lake, CA	-	Suchanek et al., 1993

# 2.5.4 Translator For Conversion Of Total Methylmercury To Dissolved Methylmercury (MeHgd/Hgt), Lotic Environments

The data and studies used by U.S. EPA for this translator are from Table 8 in Appendix B in the National Bioaccumulation Factors for Methylmercury (U.S. EPA 2000) and are presented in Table 7 in this report. Detailed discussions about each study for this table are not presented in the U.S. EPA document. The values in Table 7 ranged about five-fold (0.17 - 0.83). None of the studies took place in California; the closest study geographically was in the Carson River, Nevada (Bonzongo *et al.*, 1998). The geometric mean was 0.49, (a value similar to that found in lentic environments), indicating that about one-half of the total methylmercury is in the dissolved form in lotic environments. Filters of different pore size were used (*e.g.*, 0.20 and 0.8 μm) in some studies, which may have affected data variability. U.S. EPA (2000) did not discuss the impact of pore size on measurement of the concentration of dissolved methylmercury.

**Table 7.** Lotic Environments: Dissolved methylmercury as a fraction of total methylmercury (MeHg<sub>d</sub>/MeHg<sub>t</sub>)

MeHg <sub>d</sub> /MeHg <sub>t</sub> *	Location	Comments	Author			
0.17+	Anacostia River, MD	High flow	Mason and Sullivan, 1998			
0.32	Fox River, WI	-	Hurley <i>et al.</i> , 1998			
0.36	Hinds Creek, TN	_	D.O.E., 1997			
0.40°	Patuxent, MD	_	Benoit, 1998			
0.46	Wisconsin Rivers	Composite of 7	Babiarz <i>et al.</i> , 1998			
0.47	Sheboygan River, WI	-	Hurley <i>et al.</i> , 1998			
0.49	Grand River MI	_	Hurley <i>et al.</i> , 1998			
0.63	Pere Marquette River, MI	-	Hurley <i>et al.</i> , 1998			
0.64	Manistique River, MI	=	Hurley <i>et al.</i> , 1998			
$0.68^{+}$	Anacostia River, MD	Base flow	Mason and Sullivan, 1998			
0.68	Carson River, NV	-	Bonzongo et al., 1996			
0.80	Poplar Creek, VT	-	Campbell et al., 1998			
0.83	Wisconsin Rivers	Composite of 39	Hurley et al., 1995			
Geometric Mean = 0.49						
* Dissolved methylmercury/Total methylmercury						
+ 0.8 μm fil	+ 0.8 μm filter					
• 0.2 μm fil	• 0.2 μm filter					

# 2.5.5 Translators For Conversion Of Total Mercury To Dissolved Mercury (Hgd/Hgt), Lotic And Lentic Environments

U.S. EPA developed translators in both lentic and lotic environments for the relationship of dissolved mercury to total (physical and chemical) mercury ( $Hg_d/Hg_t$ ) of 0.60 and 0.37, respectively. U.S. EPA (2000) did not discuss how these translators might be used in the implementation plan for mercury in ambient water. It appears that this ratio may be ancillary information from the analysis for total methylmercury and dissolved methylmercury in a water sample, so it will not be discussed here in further detail.

#### 2.5.6 Translators For Estuarine Environments

U.S. EPA developed translators for this environment from very small data sets. In two cases, the ratio of dissolved methylmercury to total (physical and chemical) mercury (MeHg<sub>d</sub>/Hg<sub>t</sub>) and dissolved methylmercury to total methylmercury (MeHg<sub>d</sub>/MeHg<sub>t</sub>) data came from only two studies. Data will not be discussed individually for translators for these relationships due to small sample size. There were sufficient data in the literature to allow a derivation of the relationship between dissolved mercury and total mercury (Hg<sub>d</sub>/Hg<sub>t</sub>), but this translator is less useful. Table 8 lists the studies U.S. EPA used for this translator and the location where the studies occurred. Data are summarized from Appendix B Table 11 of the National Bioaccumulation Factors for Methylmercury U.S. EPA (2000). The translators from different studies range from 0.08 to 0.881, a difference of a slightly more than 10-fold. The geometric mean was 0.35, which indicates that about 35 percent of the total mercury (physical and

chemical) in estuarine environments in is in the form of dissolved total mercury. These data are primarily from studies outside the United States; eight of 11 studies were of water bodies in other locations in the world. One study supplied data from San Francisco Bay in California. However, the U.S. EPA (2000) has not proposed using this translator for regulatory of other purposes.

**Table 8.** Estuarine Environments: Dissolved mercury as a fraction of total mercury

0.08*					
	Elbe Estuary, Germany		Coquery and Cossa, 1995		
	3 /	_	SFEI, 1999		
	•	Surface	Mikac and Kwakal, 1997		
	•	~	Stordal <i>et al.</i> , 1996		
0.263	<u> </u>	Costal Waters	Al-Madfa <i>et al.</i> , 1994		
0.600°	/	Bottom	Mikac and Kwakal, 1997		
$0.642^{\nabla}$	Rhone, France	_	Cossa and Martin, 1991		
0.648	Operto, Portugal	Coastal Sites	Vasconcelos and Leod, 1996		
0.700*	Laptev Sea, Siberia	_	Coquery et al., 1995		
$0.780^{+}$	Chesapeake Bay, MD	-	Benoit et al., 1998		
0.881*	Kara Sea, Siberia	-	Coquery et al., 1995		
Geometric M	Mean = 0.353				
0.8 um filtra	tion, 2.5-7 m deep				
0.2 um filtration					
Uncertainty of clean techniques					
$\nabla$ 0.7 µm filtration					
	0.600° 0.642 <sup>∇</sup> 0.648 0.700* 0.780† 0.881* Geometric M 0.8 um filtra 0.2 um filtra Uncertainty	0.200 Krka River Estuary, Croatia 0.204 Galveston Bay, TX 0.263 DOHA (Qatar) 0.600 Krka River Estuary, Croatia 0.642 Rhone, France 0.648 Operto, Portugal 0.700* Laptev Sea, Siberia 0.780 Chesapeake Bay, MD 0.881* Kara Sea, Siberia Geometric Mean = 0.353 0.8 um filtration, 2.5-7 m deep 0.2 um filtration Uncertainty of clean techniques	$0.200^{\bullet}$ Krka River Estuary, CroatiaSurface $0.204$ Galveston Bay, TXCostal Waters $0.263$ DOHA (Qatar)Costal Waters $0.600^{\bullet}$ Krka River Estuary, CroatiaBottom $0.642^{\nabla}$ Rhone, France- $0.648$ Operto, PortugalCoastal Sites $0.700^{*}$ Laptev Sea, Siberia- $0.780^{+}$ Chesapeake Bay, MD- $0.881^{*}$ Kara Sea, Siberia-Geometric Mean = $0.353$ - $0.8$ um filtration, $2.5-7$ m deep0.2 um filtrationUncertainty of clean techniques		

OEHHA's review noted some concerns regarding data from the estuarine environment because in several studies, it was uncertain as to whether "clean techniques" were used in the sample work-up and analysis. Another concern was that micron filters of different porosities were used in the studies. As noted above, the impact of the filter size on the magnitude of the translator values was not discussed in the U.S. EPA's summary of these values. Apparently the filter size used by the individual investigators has not been standardized for these analyses. Standardization could make the results from the studies more comparable.

# 2.5.7 Summary Of Translators For Lentic, Lotic And Estuarine Environments

The translators derived by the U.S. EPA for three aquatic environments are shown in Table 9. These data are summarized from Appendix B Table 15 of the National Bioaccumulation Factors for Methylmercury (U.S. EPA, 2000). The translator data for estuaries for the relationships between dissolved methylmercury and total mercury and between dissolved methylmercury and total methylmercury are less robust because each was derived from only two studies, as noted above. The translator data set for estuaries for the relationship of dissolved mercury and total mercury uses 11 studies so there is some confidence in the geometric mean value of 0.35.

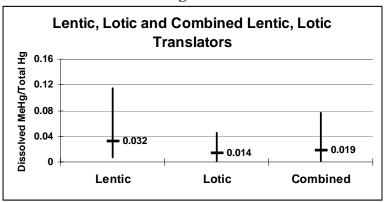
**Table 9**. Summary of U.S. EPA translators for lakes, rivers and estuaries

Mercury Species and Ratios	Lentic (Lake)	Lotic (River)	Estuary			
$\begin{aligned} &f_d \; Hg \; (Hg_d/Hg_t) \\ &f_d \; MeHg_d/Hg_t \\ &f_d \; MeHg_d/MeHg_t \end{aligned}$	0.60 0.032 0.61	0.37 0.014 0.49	0.35 0.19* 0.61*			
<ul> <li>f<sub>d</sub> Dissolved fraction</li> <li>* These translators were developed from two sites</li> </ul>						

Examination of the summary values in Table 9 shows that, on average, the translator between dissolved methylmercury and total mercury for lakes (lentic) is slightly more than two-fold (0.032 vs. 0.014) greater than the same translator for rivers (lotic), and that the same translator for estuaries is very similar to the lotic translator. The similarity between the estuary and lotic values might be expected because rivers form a part of estuary systems. The translators between dissolved total mercury and total mercury for lotic and lentic environments, which are 0.37 and 0.60, respectively, exhibit a difference of less than two-fold, and the difference between the translators for dissolved methylmercury and total methylmercury in water for lentic (0.61) and lotic (0.49) was also less than two-fold. This is somewhat unexpected given the large variability among values from individual water bodies in the database. It may be that this is a result, in part, of the reduction in variation that occurs when one uses means of means to derive a value.

In the previous discussions of bioaccumulation factors, U.S. EPA combined lotic and lentic BAFs for three trophic levels to derive national default values that could be used if local values did not exist. It seems consistent with U.S. EPA BAF methodology that the summarized translators for the relationship of dissolved mercury species to total mercury species for lotic and lentic water body types (shown in Table 9) could be combined to provide a single value for each of the three relationships. Also, the differences are not great (geometric means less than two-fold apart) and it is likely that the distributions of the translators from lotic and lentic water bodies overlap. Through combining the data for the lentic and lotic aquatic environments, the dataset would be larger and perhaps more representative of a translator for both lentic and lotic environments. Figure 3 below shows an example of combining the U.S. EPA lentic and lotic translators for conversion between dissolved methylmercury and total mercury. The bars above and below the geometric mean are the 95<sup>th</sup> and 5<sup>th</sup> percentiles of the data, respectively. This shows the high degree of overlap between values for this translator in both ecosystems. However, it should be noted that there is considerably more variability in lentic water bodies.

Figure 3



The horizontal bar is the geometric mean.

Vertical bar is the 5<sup>th</sup> to 95<sup>th</sup> percentile.

The mean values that were used to construct the figure above are shown in the Table 9.

### 2.6 CRITIQUE OF U.S. EPA MERCURY BAFS AND TRANSLATORS

U.S. EPA's stated goal for deriving national BAFs values was that they would represent long-term bioaccumulation and be applicable for as many circumstances and for as many water bodies as possible (U.S. EPA, 2000). Presumably, national translators were also intended to be as broadly applicable as BAFs. However, U.S. EPA did not test the methylmercury BAF and translator values that they derived in an effort to determine whether they met this goal. The document describing how U.S. EPA derived the national values was a draft that has not been revised or finalized as a separate document. However, U.S. EPA did include peer review comments in the document (U.S. EPA, 2000) and they did use and publish the national BAFs, including peer review comments, with the final methylmercury water quality criterion (U.S. EPA, 2001). Apparently, the national BAFs and translators met U.S. EPA's goals well enough to be used in this criterion document without any changes.

A key step in evaluating whether and how to develop regional, local, or site-specific BAFs and translators for California water bodies, and whether or when to use the national BAFs and translators in California, is to understand the limitations of the methodology and data used by U.S. EPA as well as limitations or strengths of the resulting BAF and translator values. A number of strengths, weaknesses, and limitations are described below. These include observations from the original peer reviewers, OEHHA, and other authors commenting on the U.S. EPA methylmercury criterion, BAFs, and translators.

# 2.6.1 Comments On The U.S. EPA Methodology To Derive BAFs

### 2.6.1.1 BAF Equation:

U.S. EPA used a simple ratio, equivalent to a single box model, to calculate BAFs. Theoretically, the mercury concentrations in water and fish in this model should be at steady state. There are other, more complex, models that incorporate the effects of biological, environmental, and ecological factors to estimate the accumulation of methylmercury in biota (Hope, 2003; and Kamman, *et al.*, 2003); however, these models require more information than is needed for the BAF ratio calculation. These information requirements would have further restricted the number of studies that could have been used by U.S. EPA, limiting the scope of application of the national BAFs and translators. Whether or not more complex models can be used in California will depend on data readily available for California water bodies or on designing studies that would provide these data.

The theoretical basis for the BAF equation and model has been criticized by some reviewers (AMEC-ENVIRON, 2003, and Grovhoug et al., 2003). Grovhoug et al. (2003) used data from two sampling sites on the Sacramento River and found no significant correlation between mercury in water and methylmercury in Trophic Level 3 and 4 biota, at the same site. This lack of correlation may be due, in part, to their treatment of sites as opposed to water bodies. Grovhaoug et al. (2003) looked for correlations between water and tissue concentration within single sites on this large water body. The studies used by U.S. EPA to derive BAFs averaged data across whole water bodies. In practice, no correlation is expected between a water sample and a Trophic Level 3 or 4 fish collected at the same site and time because the samples themselves represent different spatial and temporal scales. The water sample is a snapshot representation of daily conditions and single grab samples may fail to capture diurnal or hourly variation of dissolved methylmercury. The fish samples integrate conditions over a much longer period (months to years) and over a much greater space (everywhere the mobile fish has been exposed to mercury through water or food in its lifetime to date), so they cannot reflect differences in conditions for the time at which the water sample is taken. It would be more appropriate to look for correlations between mercury in water and fish across sites showing different tissue and water concentrations of mercury within a water body to see if the fish have integrated the differences in water concentrations. Some comparisons on a broader scale have shown a correlation between methylmercury in water and fish (Krabbenhoft, 1999).

#### 2.6.1.2 Dissolved Methylmercury In Water:

Overall using the dissolved methylmercury fraction in water to derive BAFs was a good choice by U.S. EPA as methylmercury is the form of mercury that bioaccumulates in the aquatic food web. Methylmercury is also the form of mercury of human health concern following fish consumption. The production, availability, and accumulation of methylmercury in aquatic food webs can be affected by a number of factors including pH, alkalinity, water temperature, sulfate concentration, dissolved oxygen, organic matter, dissolved organic carbon, landscape characteristic (*e.g.*, wetlands), and trophic structure (Brumbaugh *et al.*, 2001; Greenfield *et al.*, 2001; Harris and Bodaly, 1998; Wiener *et al.*, 2003), but clearly the amount of the dissolved

methylmercury is a potentially limiting factor at an early step in food web bioaccumulation (Kelly *et al.*, 1997; Paterson *et al.*, 1998). The chief problem U.S. EPA encountered with dissolved methylmercury to derive BAFs was that data from many studies did not measure methylmercury in water and it was necessary to convert measurements of total mercury to methylmercury using national translators.

#### 2.6.1.3 Methylmercury In Biota:

This is the best measurement to use for mercury in biota to calculate BAFs. It is the form used in the U.S. EPA tissue criterion because it is the most relevant form for human exposure via fish consumption and it is clearly associated with neurotoxicity in humans (U.S. EPA, 2001). The main problem with calculating BAFs based on methylmercury in biota is that most studies measure total mercury in this medium. This made it necessary for U.S. EPA to convert total mercury measurements in tissue to methylmercury values in tissue for various trophic levels.

### 2.6.1.4 Trophic Levels:

U.S. EPA apparently developed BAFs for Trophic Levels 2, 3, and 4 because this is part of their general strategy for developing BAFs for use in water quality criteria (U.S. EPA, 2003). U.S. EPA first developed BAFs for individual species and then combined them into trophic level BAFs. The reliability of the trophic level BAFs thus depends, in part, on accuracy in assigning species to the appropriate trophic level, as is discussed further below. While it is reasonable to calculate various trophic level BAFs because methylmercury does bioaccumulate up the food web through all trophic levels (Wiener *et al.* 2003), the role of the Trophic Level 2 BAF is unclear since no information is presented in the methylmercury tissue criterion (U.S. EPA, 2001) to show that people are consuming organisms from Trophic Level 2. The BAFs for Trophic Levels 3 and 4 are most relevant for fish species consumed by humans.

#### 2.6.1.5 Classification Scheme (Lotic/Lentic/Estuarine):

U.S. EPA did not state how they assigned the studies they used to lotic, lentic, and estuarine water body classifications. Some of the peer reviewers suggested that these classifications were too broad, and that there should be more categories based on physical, chemical, and ecological differences and similarities. One reviewer suggested the following categories: oligotrophic, mesotrophic, eutrophic lakes; estuarine (deep and shallow); open ocean; streams and rivers (high and low dissolved organic carbon); and wetlands/everglades. Using additional categories could help determine whether the national BAFs are not representative of specific environments and conditions, and identify those that fall at the extremes for bioaccumulation. However, U.S. EPA's database did not contain appropriate studies to break out categories representing all of the water body types suggested by the reviewers. Also, reclassifying water bodies into more categories would further reduce the representative data for each category. Although this was a scientifically sound idea, it would have little effect if the BAFs from all environments were still combined.

#### 2.6.1.6 Statistical Methods:

U.S. EPA used geometric means throughout their calculations of BAFs to represent the central tendency of data from studies that sometime included multiple water bodies. U.S. EPA did not discuss their choice of the geometric mean in detail. They state that geometric means were used for convenience and because the factors underlying BAF variability were believed to be multiplicative and the data sets log normally distributed (U.S. EPA, 2000). However, they did not present the distributions of the data they used or show statistical tests demonstrating that these data were log normal. One reviewer suggested that they provide a more detailed explanation of their rationale and provided some possible language. Another suggested that means could have been calculated for individual water bodies rather than using a single mean for all water bodies in the same study.

Arithmetic means could be used rather than geometric means to represent the central tendency of data when calculating BAFs. Arithmetic means generally yield higher values than geometric means. OEHHA favors using arithmetic means in human health assessments and fish consumption advisories because they are more health protective. Using arithmetic means to calculate the data summaries for methylmercury concentrations in biota and water that are used to calculate BAFs from individual studies might have little effect on the BAF values at this level. However, using arithmetic means to calculate means from studies and means after merging lentic and lotic BAFs would likely result in higher final national BAF values. BAFs based on arithmetic means are likely to yield higher tissue concentrations from the same water concentration than BAFs based on geometric means. Conversely, if BAF values are used to convert back to water concentrations, BAFs based on arithmetic means are likely to yield lower water concentrations from the same tissue concentration than BAFs based on geometric means.

Ideally, the distribution of the data sets used in BAF calculations should be tested to determine whether they are log normally distributed before choosing to use geometric means. This cannot be done for the national BAFs without the entire database, but it is recommended for any attempts to derive BAFs based on data from California water bodies.

# 2.6.1.7 Combining Lotic And Lentic Classifications Into Single National BAFs For Trophic Levels:

U.S. EPA based merging lentic and lotic BAFs on a qualitative rather than quantitative comparison of BAF values. They combined BAFs because the data ranges overlapped. As a result, the variability within each BAF was very large. The merging of lotic and lentic datasets to derive a single national BAF generated considerable discussion by the peer reviewers. Reviewers suggested that, instead of merging the lentic and lotic datasets for the calculation of BAFs, lentic and lotic environments should be split into more ecological categories that better reflect the aquatic chemistry of each environment. Although peer reviewers recognized U.S. EPA's purpose in deriving a single BAF, most disagreed with combining BAFs and advocated for developing separate BAFs for more environments, especially at the regional or local level. Developing specific BAFs for various categories of California water bodies (*e.g.*, lentic, lotic, and estuarine) would be consistent with this recommendation. It would also provide an

opportunity to compare the California values with the national values to see if they are really different and to look for water body characteristics associated with very different BAF values.

# 2.6.1.8 Standard Techniques:

Standard techniques were not used in the retrospective database compiled by U.S. EPA. Many of the peer reviewers suggested that using standard methods and uniform protocols would improve the study design and resulting data quality. This is especially true for determination of dissolved methylmercury. Different filter pore sizes were used by different researchers to separate the dissolved fraction of mercury or methylmercury in some of the studies used by U.S. EPA. As a result, some of the data for dissolved mercury or methylmercury could include some mercury bound to organic carbon or colloids. Standard sampling periods for water samples and standard ranges for fish lengths or edible sizes were not used and differences in these methods could also contribute to variation in the resulting BAFs. Standardized techniques would be essential for water and tissue measurements used in regulations.

# 2.6.2 Comments On The U.S. EPA Methodology To Derive Translators

### 2.6.2.1 Translators For Water:

U.S. EPA derived translators to convert other forms of mercury in water to dissolved methylmercury in order to calculate BAFs in a consistent manner. Again, U.S. EPA used a simple ratio between forms to calculate each translator. The translator conversion factors for water assume that there is a linear relationship between the various forms of mercury in water. This may be an over-simplification, especially of the relationship between total mercury and methylmercury in water. Methylmercury concentrations, in particular, are affected by other factors, *e.g.*, microbial communities, temperature, sulfide, and redox conditions (Ullrich *et al.* 2001), and high or low methylmercury values may not correlate well with total mercury values (Monson and Brezonik 1998; Gilmour *et al.* 1998). Many peer reviewers expressed reservations about using translators between total and methylmercury in water, and suggested that these be developed on a more local or site-specific basis. As noted in the discussion of the BAF method, the lack of standardized methods, especially standard pore sizes for determining dissolved mercury forms, may affect the variability in data used to calculate translators, as well as BAFs.

#### 2.6.2.2 Translators For Biota:

U.S. EPA derived translators for biota to convert total mercury measurements in tissue to methylmercury values in tissue. This was fairly straightforward for higher trophic level fish (Trophic Level 3 and 4) where the conversion based on the assumption that nearly 100 percent of total mercury is methylmercury is well accepted, health protective, and consistent with most monitoring programs. U.S. EPA derived additional conversion factors for Trophic Level 2 organisms in lentic and lotic water bodies. The reliability of the Trophic Level 2 translators depends on whether the organisms used are representative of all Trophic Level 2 organisms, and whether U.S. EPA accurately assigned species to Trophic Level 2. This is discussed further below.

#### 2.6.2.3 Separating Water Body Types:

U.S. EPA developed and retained separate translator values for lentic, lotic and estuarine water bodies. They did not explain why they did this but later combined the BAFs derived from them. Peer reviewers were in favor of separate lentic and lotic translators, and suggested that some of the water bodies in these separate classifications were actually at environmental or ecological extremes and should not be combined with other data to derive translators.

#### 2.6.2.4 Other:

As noted in the BAF methodology discussion, U.S. EPA used geometric means to calculate translators because environmental variables tend to be log normally distributed. However, they did not show that the underlying data were log normally distributed or discuss their rationale in detail. The reviewers commented on this and one also suggested that means could have been calculated for individual water bodies rather than using a single mean for all water bodies in the same study.

#### 2.6.3 Comments On The Data U.S. EPA Used To Derive BAFs

### 2.6.3.1 Representativeness Of Water Bodies In The Database:

It is not clear whether the water bodies from the studies used by U.S. EPA are representative of the range of water body types in the United States. U.S. EPA did not include specific physical and chemical information on the water bodies that might be useful in categorizing them. Many of the studies used are for seepage lakes in the Midwestern United States, whose primary source of mercury is atmospheric deposition. Conditions and BAFs from these water bodies may be different than in California water bodies where the primary source of mercury, in most cases, is gold or mercury mining. In fact, some of the peer reviewers recommended not using the data from Clear Lake, California because this site was not "typical" and had an unusual BAF. They felt that Clear Lake was not typical at the national level because its main source of mercury was runoff from a former mercury mine instead of atmospheric mercury. But legacy mining is a typical mercury source in California so these data may be especially relevant for California water bodies. Reviewers also questioned using data from other areas with unique conditions or high contamination, and they questioned U.S. EPA's inclusion of wetland data as a lotic ecosystem. U.S. EPA used international data but did not explain why they were merged with U.S. data. Using these data did broaden their database on which BAF calculations were based, however, it might also have introduced data from water bodies with variations in abiotic and biotic factors very different than those in the United States. The Papina et al. (1995) study from Russian was one of the studies the peer reviewers suggested had questionable data. In retrospect some reviewers were focused more on potential water body differences in physical, chemical, or ecological conditions than on U.S. EPA's attempt to derive broadly representative BAF values. These differences in perspective can only be resolved by deriving better local or regional BAFs.

# 2.6.3.1 Quality Assurance:

One problem with the study data was that standard collection and analytical techniques were not used. The peer reviewers commented on this and the necessity of using well-defined techniques in particular for the assessment of methylmercury in water because it is difficult to measure due to its low concentrations in water (e.g., from  $10^{-6}$  to  $10^{-9}$  mg/L). U.S. EPA dealt with the nonstandard analytical techniques, in part, by applying a set of analytical QA criteria to the chemistry data from the studies they selected. Using QA criteria increased the precision and reproducibility of the chemistry results, but had the effect of excluding studies relying on methylmercury data in water analyzed before 1990, although some studies containing total mercury results in water were included. This did not solve all problems associated with the lack of standard techniques. The peer reviewers pointed out some water data that U.S. EPA used that they felt were unreliable. Among the studies mentioned were data from Papina et al. (1995) where the methylmercury concentration was unusually high; data of Glass et al. (1990 and 1992) where the measured concentrations were very low; data from Jackson et al. (1991) that included data from the early 1980's using non-contemporary methods; data from Mason and Sullivan (1997) who reported values at the detection limit of the analytical method; data from Monson and Brezonik (1998 and 1999) who used a different method to measure mercury forms; and the study by Stober et al. (1995) where QA/QC issues were discovered after its inclusion in the U.S. EPA set. The peer reviewers felt that using data from these studies might affect the overall quality of BAF values calculated from them.

The peer reviewers also raised issues concerning the collection and interpretation of plankton and seston data noting that some samples were potentially a mixture of trophic levels (Trophic Level 1 and 2) and phylogenetically different organisms. These problems would impact the BAFs for Trophic Level 2.

## 2.6.3.3 Trophic Level Classification:

It is not clear if the number and kind of species from the studies used to derive each trophic BAF are representative of species in water bodies across the U.S. and those in California. Furthermore, the functional trophic level of a species can vary between water bodies and regions and this could lead to misclassifications of data assigned to a trophic level (e.g., in lakes King salmon eat like Trophic Level 4 organisms, but in rivers they eat like Trophic Level 3 organisms). Trophic Level 2 organisms from the U.S. EPA studies included phytoplankton, zooplankton, microseston, mosquito fish, and stone rollers (see Table 10). Phytoplankton are Tropic Level 1 organisms, and microseston might include some primary producers, but it can be hard to separate these from zooplankton. Similar organisms are likely to be found in California. However, none of the studies included potential Trophic Level 2 organisms such as clams, mussels, crayfish, or crabs that might be harvested and eaten from water bodies in California. Although U.S. EPA has included Trophic Level 2 organisms in their water quality criteria it is not clear whether organisms at this level contribute significantly to human exposures in California. Peer reviewers questioned the assignment of mosquito fish to Trophic Level 2 rather than Trophic Level 3. Trophic Level 3 organisms from the U.S. EPA studies included shiner, perch, carp, shad, silversides, bluegill, sunfish, and juvenile bass species, which might also be found at this trophic level in California. The U.S. EPA studies did not include any trout, salmon

or catfish species in this trophic level. In California, some species of these fish are likely to be at this trophic level and these are also important game fish (*i.e.*, fish that anglers catch and consume). Trophic Level 4 organisms from the U.S. EPA studies included largemouth bass and other bass species, lake trout, walleye, northern pike, and burbot. In California, largemouth bass and other bass species are likely to be at this trophic level and some brown trout, catfish, or lake salmon may be as well. Including a more complete cross-section of data for species relevant to California consumers would improve the relevance of the trophic level BAFs. California data should be investigated to see if this is possible.

Table 10: Biota used by U.S. EPA to calculate BAFs for Trophic Level 2, 3, & 4

Trophic Level 2	Trophic Level 3	Trophic Level 4
Microseston	bass (juvenile)	bass
Mosquito fish	bloater	largemouth bass
Phytoplankton	bluegill	smallmouth bass
Stone roller	bream	burbot
Zooplankton	carp	lake trout
•	dace	northern pike
	gizzard shad	pike
	grayling	walleye
	Johnny darter	•
	Mayan cichlid	
	perch	
	perch/roach mix	
	log perch	
	yellow perch	
	redbreast	
	roach	
	shiner	
	spottail shiner	
	emerald shiner	
	spotted shiner	
	silversides	
	spotted sunfish	
	spotted tilapia	

Species lists from U.S. EPA (2000).

# 2.6.3.4 Standard Techniques:

The lack of standardized methods increases variability and decreases reproducibility of the water and fish data compiled by U.S. EPA. Sampling periods, fish age and size, and analytical preparation techniques (*e.g.* whole fish vs. fillet) differed among studies. For example, in some cases, water data were based on single grab samples while seasonal composite samples were taken in others. Thus some sampling incorporated seasonal variation while other sampling excluded it.

# 2.6.3.5 Compiled Data:

It is not possible to determine the actual sample size for fish and water measurements in the database compiled by U.S. EPA because the sections of the report (U.S. EPA, 2000) available to OEHHA only include summaries of the studies from which data were entered into the database. The existing database compiled by U.S. EPA is acceptable for developing broad-based BAFs despite the limitations discussed. However, as noted by the peer reviewers, the underlying spread of data may not yield BAFs that are practically very useful. The peer reviewers unanimously supported collecting more and better quality data, especially on the local and regional level. These data would be more applicable for local or regional conditions and would likely be less variable than the broad-based national data.

#### 2.6.3.6 Other Studies:

The peer reviewers compiled lists of additional studies that they suggested U.S. EPA consider including to derive BAFs. Some of these studies were for California water bodies, and additional studies have been published in the past several years. These studies could potentially be used to derive BAFs based on California specific data.

## 2.6.4 Comments On The Data U.S. EPA Used To Derive Translators

## 2.6.4.1 Quality Assurance:

As discussed above, the lack of standard techniques (*e.g.*, using different pore size filters) to separate the dissolved fraction of mercury increases the variability and decreases the reproducibility of derived translators. Some of the study data could include mercury bound to dissolved organic carbon or colloids, while others do not. Since mercury in water can vary seasonally, non-standard sampling could also increase variation if data from different seasons were used to derive translators.

Also as noted above, reviewers suggested that data from some water bodies (*e.g.* Clear Lake, California, and others) be excluded from the U.S. EPA database because of the high total mercury, but low methylmercury concentrations in water. These studies also yielded high translator relationships, which may bias the current translator values. These studies, however, may be relevant in California where total mercury concentrations in water bodies may be higher due to mining sources.

The general comments above on the BAF data concerning representativeness of water bodies in the database, standard techniques, compiled data, and other studies are also applicable to the translator data.

#### 2.6.5 Comments On The U.S. EPA National BAF Values

# 2.6.5.1 Gaps in Available Data

There were not enough good data available to U.S. EPA at the time they compiled their database to develop estuarine BAFs. This is a significant data gap for California because the San Francisco Bay-Delta is a huge estuary draining about 60-70 percent of the runoff from the Sierra Nevada Mountains. SWRCB should investigate compiling data from this estuary and/or other California estuaries to develop water body specific or a California default BAF for estuaries.

# 2.6.5.2 Variability

Table 11 shows the direct, converted, and combined BAFs developed by U.S. EPA for different trophic levels and water body types. The minimum, maximum, and geometric means for the studies compiled by U.S. EPA are given in the table. In order to get some measure of the data variation within each category, the maximum value is divided by the minimum value and shown in the table as the "fold variation." Standard deviation or the coefficient of variation would be better measures of variability but these cannot be calculated without the complete database. These simple calculations give some idea of the inherent variability in the BAF values.

Table 11: Relative variability in BAFs for lentic and lotic Trophic Level 2, 3, & 4

	BAF Trophic Level 2		BAF Trop	hic Level 3	BAF Trop	BAF Trophic Level 4	
Direct BAFs	Lentic	Lotic	Lentic	Lotic	Lentic	Lotic	
minimum	42,400	34,474	504,000	334,325	4,000,000	985,915	
mean	85,600	178,678	1,260,000	1,636,298	6,800,000	2,524,477	
maximum	172,764	608,728	4,170,000	11,250,000	11,400,000	6,464,028	
Fold variation	4	18	8	34	3	7	
Converted							
<b>BAFs</b>							
minimum	61,757	8,661	734,095	35,238	3,954,284	96,905	
mean	149,960	62,000	1,330,000	346,613	4,100,000	1,380,361	
maximum	326,264	260,811	3,262,643	1,499,688	4,203,000	10,401,681	
Fold variation	5	30	4	43	1	107	
Combined							
<b>BAFs</b>							
minimum	34,	474	35,	238	96,	905	
mean	117,000		680	,000	2,670	0,000	
maximum	608	,728	11,25	60,000	11,400,000		
Fold variation	1	8	3	19	1	18	

Minimum and maximum values are the mean values for the species with the lowest and highest BAF, respectively, for each water body type and indicated trophic level.

Mean values are geometric means from U.S. EPA (2000).

Examination of direct BAFs in the table showed that, for Trophic Level 2, the lotic mean and maximum are higher than the lentic mean and maximum values, but the lotic minimum was less than the lentic. This same pattern was seen for Trophic Level 3. However, for Trophic Level 4 the lentic mean and maximum values were higher than the same lotic values, and the lentic minimum was also higher than the lotic minimum. Although the trophic level pattern of BAF values was not consistent, the lotic BAFs at all trophic levels were consistently more variable based on the ratio of the maximum and minimum values. All of the lentic values show less than an order of magnitude difference, while the values for Trophic Levels 2 and 3 in lotic water bodies show greater than an order of magnitude difference.

Examination of the converted BAFs show a different pattern of high and low values for trophic levels in lentic and lotic water bodies, but a similar pattern for variation. In this case, for Trophic Level 2, the lentic mean, maximum, and minimum values are greater than the corresponding lotic values. The same pattern is seen in Trophic Level 3. In Trophic Level 4, the mean and minimum values are higher than the lotic, but the maximum value is lower. Some of the differences between direct and converted BAFs are likely to be due to effects of using translators to convert measured values. But, in all cases, the lotic BAF values are again more variable; all show more than an order of magnitude variation, and all show more variation than for direct BAFs. Lentic values, however, all show less than an order of magnitude variation, and the level of variation is similar to that seen for direct BAFs.

As seen in Table 11, combining the direct and converted BAFs for lentic and lotic water bodies to derive the national default values either retains or increases the variability from the underlying data. U.S. EPA calculated the 5<sup>th</sup> and 95<sup>th</sup> percentile ranges for BAFs at each trophic level in lentic and lotic water bodies and for the combined national BAFs. The lower and upper bounds also show the same pattern of variability demonstrated above: lotic BAFs are more variable than lentic, and lotic BAFs show greater than an order of magnitude difference between upper and lower bounds.

One way to decrease the inherent variability when using BAFs would be to use the direct BAFs for each trophic level and water body type, rather than using the U.S. EPA default values. SWRCB should investigate compiling data to derive California specific direct BAFs for lentic, lotic and estuarine water bodies, and other water body types of potential interest. This could be especially important because the primary source of mercury in most California water bodies is different than the atmospheric source in most of the studies U.S. EPA used to derive BAFs.

## 2.6.6 Comments On The U.S. EPA National Translator Values

# 2.6.6.1 Gaps in Available Data

U.S. EPA did develop three translators for estuarine water bodies. However, the translators between dissolved methylmercury and total mercury and dissolved methylmercury and total methylmercury were based on a relatively small sample size. Good estuarine translators are important in California because of the San Francisco Bay. SWRCB should investigate compiling

data to derive translators for San Francisco Bay and/or other California estuaries and water body types.

## 2.6.6.2 Variability

Table 12 shows national translator values for lentic and lotic water bodies and one based on more data for estuarine water bodies. The minimum, maximum, and geometric means for the studies compiled by U.S. EPA are given in the table. In order to get some measure of the data variation within each category the maximum value is divided by the minimum value and shown in the table as the "fold variation." Standard deviation or the coefficient of variation would be better measures of variability but these cannot be calculated without the complete database. These simple calculations give some idea of the inherent variability in the translator values.

Table 12: Relative variability in lentic, lotic, and estuarine translators

Translator	МеНд	d/Hgt	MeHgd	/MeHgt	Hgd/Hgt
Water body	Lentic	Lotic	Lentic	Lotic	Estuarine
Minimum	0.002	0.002	0.303	0.17	0.08
Mean	0.032	0.014	0.613	0.49	0.353
Maximum	0.139	0.051	1.02	0.83	0.881
Fold variation	70	26	3	5	11

MeHgd = dissolved methylmercury; MeHgt = total methylmercury; Hgd = dissolved inorganic mercury;

Hgt = total mercury

Mean values are geometric means from U.S. EPA (2000).

Examination of this table shows that lotic translators have lower minimum, mean, and maximum values than translators for lentic environments. Estuarine values are similar to lotic, but are not directly comparable because they are not for the same forms of mercury as the lentic and lotic translators. The greatest variability, based on the ratio of maximum and minimum values, is seen for the translator between dissolved methylmercury and total mercury. Variability for this translator is more than an order of magnitude, similar to the variability for the estuarine translator between dissolved mercury and total mercury. Variability for the translator between dissolved methylmercury and total methylmercury is less than an order of magnitude.

Using translators to convert other mercury forms to dissolved methylmercury increases the variability in BAF calculations. Analytical methods to measure methylmercury have improved so future studies would be wise to always measure dissolved methylmercury directly, reducing the need to use translators. SWRCB should investigate compiling data or conducting new studies to derive default translators for a variety of California water bodies. This is especially important because the primary source of mercury in most California water bodies is legacy mercury or gold mining, which is different than the atmospheric source in most of the studies in the U.S. EPA database used to derive translators.

# 2.7 CONCLUSIONS CONCERNING U.S. EPA's DEVELOPMENT OF BAFs AND TRANSLATORS

National BAFs and translators have a number of flaws, owing largely to their derivation from a database that was compiled retrospectively from available studies. A well-designed, prospective study using standardized methods and stratified random sampling of specific types of water bodies might generate data that is less variable and possibly more useful for examining factors affecting mercury bioaccumulation for a broad scale of water bodies. Generating data using standard protocols would remove the influence of variation due to study methodology so that the effects of limnological and environmental variables could be determined. It would also require years to plan and complete but potentially yield information that could be practically applied. The external peer reviewers for the U.S. EPA document (U.S. EPA, 2000) were strongly in favor of collecting additional, higher quality data to use for BAFs and translators. To develop standard methods, factors such as the optimal sampling period for water and fish need to be determined, as well as where samples should be collected in the water column, and whether to do grab or composite samples. Standardized size or age ranges for fish or specific species to be collected for each trophic level should also be developed. The spatial relationship between fish and water samples also needs to be established for water bodies or "sites." In fact, the concept of "sitespecific BAFs" should be examined. It is unlikely that BAFs for a specific site, such as a marina dock, or a specific latitude and longitude determined by GPS can be developed. Data can be collected to develop BAFs for larger water bodies (e.g., Clear Lake, or Cache Creek) or perhaps segments of longer rivers (e.g., the Sacramento River above Lake Shasta). The BAFs U.S. EPA developed were essentially for water bodies, not sites.

Despite these problems, the national default values for BAFs and translators were developed in a methodical manner using the best available data. These values were not tested by U.S. EPA to see how well they would predict tissue or water concentrations. This should be done to demonstrate and test their practical application, prior to using them in a policy to implement the methylmercury tissue criterion, using some criterion for goodness of fit to empirical data. Using the directly calculated BAFs (those based on measured dissolved methylmercury in water) for lentic and lotic water bodies separately can be considered as an alternative to the combined national default values. These values are less variable than the combined national values, and do not include the additional uncertainty added by using water translators and combining water body types. However, they are based on a smaller dataset. As another alternative, the California SWRCB could compile data on concentrations of mercury in fish and water for California water bodies to see if regional or local BAFs and translators could be derived that have less variability than the national values. Ideally, information on other factors known to affect methylmercury bioaccumulation (e.g., pH, alkalinity, water temperature, sulfate concentration, dissolved oxygen, organic matter, dissolved organic carbon, landscape characteristic, and trophic structure) could be collected for these water bodies to aid in future classification of differences in BAFs in different types of California water bodies.

# 3 DERIVATION OF CALIFORNIA-SPECIFIC BAFs AND TRANSLATORS FROM THE SWRCB DATABASE

The State Water Resources Control Board (SWCRB) contracted with Science Applications International Corporation (SAIC) to compile water and biota mercury concentration data for California water bodies in an Access database titled "California Mercury Ambient Water Quality Criteria." This database contains information on water and biota data for lentic, lotic and estuarine environments. OEHHA used an Excel file version of this database 6 (refered to as the SWRCB database in this report) for this evaluation. For each of these environments, BAFs were calculated for three trophic levels in three aquatic environments, hence nine BAFs were reported in the database.

The discussion that follows will:

- 1) compare U.S. EPA and SAIC methods for calculating BAFs. This will include a brief discussion of the data in the SWRCB and U.S. EPA databases that were used to calculate BAFs.
- 2) describe an alternate method to calculate BAFs from the California data in the SWRCB database. This method will be used to make the California calculations as similar to those by U.S. EPA as possible within limits of the California data collection method. These alternative California-specific BAFs will be compared to BAFs derived by U.S. EPA.
- 3) investigate the SWRCB database for California water bodies to determine whether it is possible to develop translators for some aquatic environments. These California-based translators will be compared to translators derived by U.S. EPA.

## 3.1 U.S. EPA DATABASE FOR CALCULATION OF BIOACCUMULATION FACTORS

As previously noted, U.S. EPA carefully selected studies for inclusion in the database it used to calculate lentic and lotic BAFs. Studies had to meet certain standardized criteria for analytical chemistry data (*e.g.*, be reproducible and have a low detection limit and minimal matrix interferences) as specified in National Bioaccumulation Factors for Methylmercury (U.S. EPA, 2000). These rigorous criteria selected for high quality data, but only a limited number of studies met them and were thus included in the U.S. EPA database. In addition, U.S. EPA only included data from studies in which the same author or authors collected and measured some form of mercury in both biota and water in the same water body as part of the same investigation. These measurements, while for the same water body, were not necessarily collected at the same time or at the same site as defined by GPS coordinates. Sometimes data for water and/or biota mercury concentrations were aggregated over several years for the same water body or site by authors in the selected studies. Table 13 shows the number of studies from which U.S. EPA extracted the data entered in their database. U.S. EPA's calculations of BAFs and translators from this database have already been discussed.

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<sup>&</sup>lt;sup>6</sup> The database referenced in this document is dated March 2004 and referred to as the SWRCB database.

The U.S. EPA database was not available for OEHHA to determine the true number of samples and measurements included in it. Far more samples were included in the database than shown by the number of studies because some of the studies involved many water bodies and/or used data from multiple replicate measurements of mercury in biota and water in each water body. For example, Watras *et al.*, (1998) studied 15 lakes in Wisconsin that were entered in the U.S. EPA database and used to calculate the BAFs. The replicate measurements within and among water bodies from each study are not evident because U.S. EPA first reduced the water and biota measurements to a single BAF for each trophic level in a study and then to a single BAF for each environment.

**Table 13.** Number of studies in the U.S. EPA database used to derive national BAFs<sup>+</sup>

Trophic Level:	2	3	4
Environment			
Lentic			
Direct	2	5	4
Converted	5	4	2
Total	7	9	6
Lotic			
Direct	3	6	2
Converted	3	15	5
Total	6	21	7

Data from Tables 5-1 (lentic) and 5-2 (lotic), U.S. EPA, 2000
 Direct: dissolved methylmercury concentration was measured in study;
 Converted: the mercury form measured in water was converted into dissolved methylmercury by using the national translators derived by U.S. EPA (2000).

## 3.2 CALIFORNIA SWRCB DATABASE AND METHOD FOR CALCULATION OF BAFS

Table 14 summarizes information on California biota and water data contained in the Excel file used by OEHHA that contained the SWRCB dataset. SAIC entered mercury measurements for water and biota collected in California by various researchers but did not use the same criteria that U.S. EPA did when compiling their database (see Appendix 1 for criteria for SWRCB database). Unlike the U.S. EPA database data entries were not restricted to studies in which water and biota from the same water body were measured in the same study. The dataset for the lotic environment contained the most entries for both water and biota, with more than 100 entries (see Table 14) for each trophic level. The lentic environment had the fewest entries for water measurements and these were all from one water body, Standish Dam, which did not include any measurements of mercury in biota. The lentic environment also had the fewest entries for Trophic Level 2 biota, but contained a large number of Trophic Level 3 and 4 biota data.

Table 14. Number of data entries in the SWRCB database#

•	Water Entries		<b>Biota Entries</b>	
Environment	Water*	Trophic Level 2	Trophic Level 3	Trophic Level 4
Lentic	11	9	345	814
Lotic	474	110	622	1224
Estuarine	306	211	25	240

<sup>\*</sup> Data were reported for various forms of mercury. They were converted to dissolved methylmercury (DMeHg) for the purpose of calculating BAFs. The conversion to dissolved methylmercury was accomplished by using the national translators developed by the U.S. EPA.

The SWRCB database was a compilation of studies for California water bodies that were reported by different investigators. Because, as noted above, the SWRCB California database was not restricted to matching biota and water samples from the same study and investigators, the compiled data, even when from the same water body, might be more variable than that in the U.S. EPA database due to differences in analytical methods or data quality. This might be expected to lead to differences between BAFs calculated from the SWRCB California and U.S. EPA databases.

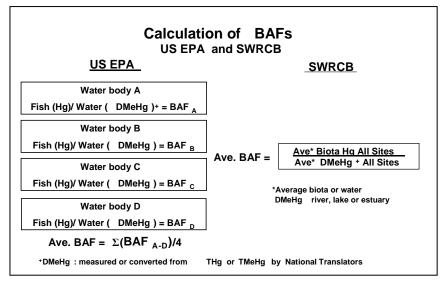
SAIC used the standard BAF equation to calculate BAFs from the SWRCB California database. A concentration for methylmercury in biota was divided by a concentration for dissolved methylmercury in water. SAIC also used the national translators developed by U.S. EPA to convert water data reported as total mercury or total methylmercury to dissolved methylmercury when calculating BAFs. SAIC calculated nine statewide BAFs (three environments and three tropic levels) using the data they compiled. However, SAIC calculated BAFs from the SWRCB California database somewhat differently than that used by U.S. EPA to calculate the national BAFs.

In the Excel file SAIC used all biota and water data for each aquatic environmental type (*e.g.*, lentic) and trophic level entered in the SWRCB California database to calculate a statewide arithmetic mean value for biota and water, respectively, and then calculated a corresponding BAF from these overall means for each trophic level and environment. This process is not mathematically equivalent to the method employed by U.S. EPA. U.S. EPA first calculated mean biota and water concentrations of mercury for individual water bodies and/or studies and then calculated a BAF for the water body and/or study at each trophic level. The BAFs from multiple water bodies were averaged by U.S. EPA to derive single national values for each trophic level and aquatic environment. The SAIC method yields a point estimate for each BAF (*i.e.*, the BAF is based on one mean value in the numerator and denominator, not a sum of means from each). Consequently, it is not possible to derive information on the variability (standard deviation, etc.) of their California statewide-BAFs. In contrast, it is possible to calculate variability using the U.S. EPA method. Without repeated measures and estimates of variability it is not possible to statistically compare the SAIC BAFs with those derived by U.S. EPA. Figure 4

<sup>#</sup> The March 2004 version of the SWRCB database was used.

illustrates the methods used by the U.S. EPA and in the Excel file of the SWRCB dataset for calculation of BAFs.

Figure 4. Comparison of U.S. EPA and SAIC methods for calculation of BAFs from U.S. EPA and SWRCB datasets



U.S. EPA used fish and water data from one water body at a time to calculate a BAF for each water body (*e.g.*, water bodies A, B, C, and D). Then U.S. EPA summed these BAFs and averaged them. U.S. EPA initially did this for all three trophic levels in each type of water body. In the SWRCB Excel file dataset, SAIC summed all of data for mercury in fish from all of the water bodies of one kind in the California database they compiled and averaged the mercury concentrations. Next, they summed all of data for mercury in water from all of the water bodies of one kind in the California database they compiled and averaged the mercury concentrations. They then calculated a BAF from these grand averages. This was done for all three trophic levels in each type of water body.

# 3.3 ALTERNATIVE METHOD FOR THE CALCULATION OF BAFs IN CALIFORNIA

An alternative method was investigated for calculation of BAFs using the SWRCB California database. This method is similar to that used by U.S. EPA and allows for calculation of water body-specific BAFs. A preliminary survey of the three aquatic environments in this database indicated that the lotic environment contained sufficient water and biota data to use this method to calculate water body-specific BAFs. U.S. EPA used geometric means to calculate BAFs, but arithmetic means will be used for the alternate California method. Arithmetic means were used because they are more health protective than geometric means (*i.e.*, they are higher numerically) and because, in many cases, the available samples size from an individual water body was too small to test the statistical form of the data distribution. In order to use this alternative method for estimation of BAFs for California water bodies, the following unweighted arithmetic means were calculated:

1) **Numerator:** arithmetic mean mercury concentrations in biota from a water body (*e.g.*, San Joaquin River, Sacramento River, etc.) were calculated for each trophic level (2-4). Most mercury concentrations in biota (Trophic Levels 3, 4) were derived from measurements of

wet tissue samples. Since a few samples in Trophic Level 2 were dried prior to analysis, these data were converted to wet-weight mercury concentrations by using U.S. EPA translators (U.S. EPA, 2000).

2) **Denominator:** arithmetic mean mercury concentrations of dissolved methylmercury were calculated for a water body (*e.g.*, San Joaquin River, Sacramento River, etc.) matching the biota data. Measured dissolved methylmercury and concentrations converted from total mercury or methylmercury were used in this calculation. The U.S. EPA's national translators were used for the conversion of these data to dissolved methylmercury concentrations.

This alternative BAF methodology applied to data selected from the SWRCB California database aggregates biota and dissolved methylmercury concentrations, respectively, from a water body to calculate a BAF for one water body at a time. This aggregation is logical since dissolved methylmercury levels from the same water body are more likely to be similar than those from geographically separated water bodies (*e.g.*, for lakes in northern and southern California). And the same is true of aggregated biota concentrations for the same water body.

# 3.3.1 Application of the Alternate Method to Calculate BAFs from Data in the SWRCB California Database

This section describes the mercury levels in biota and dissolved methylmercury in water in ten rivers in California from the SWRCB California database and derives BAFs based on these data. These rivers will be used because they are the only rivers in the database that have both measurements of mercury in water and in fish. It should be noted that the ten rivers in the database are not a random sample of California rivers; they fall predominantly in the Sacramento-San Joaquin-San Francisco Bay Delta watershed.

# 3.3.1.1 Biota Data For Ten Rivers In California

Table 15 contains available information on the concentrations of mercury in Trophic Level 2 biota from the SWRCB California database found in four out of the ten rivers for this trophic level. Concentrations range from a low of 0.013 mg/kg in Putah Creek to a high of 0.018 mg/kg in the Sacramento River, a less than two-fold variation. The values of the arithmetic mean and the median concentrations are similar for the data, suggesting that they may be normally distributed, but the sample size is too small to test this for individual water bodies. Although data for individual water bodies are not very variable (*e.g.*, the standard deviation in all cases is less than the mean), the sample sizes are low (5-11 samples per water body) and additional data for all rivers would need to be collected to have more representative samples of mercury concentrations in Trophic Level 2 organisms in California rivers.

**Table 15.** Concentrations of methylmercury (mg/kg) in Trophic Level 2 biota<sup>+</sup>

Water Body	Arithmetic Mean	Standard Deviation	Median
Sacramento River (6)*	0.018	0.013	0.011
Mokelumne River (0)	-	-	-
Putah Creek (5)	0.013	0.004	0.013
San Joaquin River (0)	-	-	-
Napa River (11)	0.015	0.006	0.014
Bear River (0)	-	-	-
Coyote Creek (0)	-	-	-
Guadalupe River (0)	-	-	-
Alamo River (0)	-	-	-
Redwood Creek (9)	0.015	0.008	0.013

<sup>+</sup> Methylmercury was assumed to be 49 percent of total mercury in Trophic Level 2 biota

Table 16 summarizes the available mercury concentrations for Trophic Level 3 biota from nine rivers in the SWRCB California database. There are no available data for Redwood Creek. Only the Sacramento and San Joaquin River had more than ten samples. The mercury concentrations range from a low of 0.06 mg/kg in the Alamo River biota to a high of 0.53 mg/kg in fish from the Guadalupe River. The arithmetic mean and the median concentrations are similar in six out of nine cases suggesting that the data may be normally distributed for these rivers, but the sample sizes are too low to test this for individual water bodies. The mean and median are dissimilar in three cases (Sacramento, Bear, and Guadalupe River); however, the sample size for the Bear and Guadalupe Rivers is small, so this should not be over-interpreted. In seven out of nine cases, biota concentrations for individual water bodies are not very variable (e.g., the standard deviation is less than the mean). But the sample sizes are low (2-10 samples per water body, and 32 for the San Joaquin River). The Sacramento River, which has the most samples, also has the greatest standard deviation. Based on these limited data, more differences in mercury bioaccumulation are shown by Trophic Level 3 biota in the Sacramento River. This is not surprising given the changes in the river ecosystem between the beginning and end of the Sacramento River. Overall, additional data for all rivers would need to be collected to have more representative samples of mercury in Trophic Level 3 organisms in California rivers.

<sup>\*</sup> Number of samples collected

**Table 16.** Concentrations of methylmercury (mg/kg) in Trophic Level 3 biota<sup>+</sup>

Water Body	Arithmetic Mean	Standard Deviation	Median
Sacramento River (45)*	0.34	0.45	0.17
Mokelumne River (9)	0.31	0.14	0.31
Putah Creek (10)	0.13	0.04	0.13
San Joaquin River (32)	0.14	0.07	0.12
Napa River (6)	0.26	0.09	0.26
Bear River (2)	0.21	0.21	.0.04
Coyote Creek (5)	0.14	0.06	0.11
Guadalupe River (5)	0.53	0.48	0.20
Alamo River (5)	0.06	0.02	0.06
Redwood Creek (0)	-	-	-

<sup>+</sup> Methylmercury was assumed to be 100 percent of total mercury in Trophic Level 3 biota

Table 17 summarizes the available data on mercury concentrations in Trophic Level 4 biota from seven rivers in the California database. No data were available for Trophic Level 4 for Napa River, Coyote Creek or Redwood Creek. Compared to Tropic Levels 2 and 3, the number of samples collected for Trophic Level 4 is significantly larger. Of the rivers with data, only the Alamo River had fewer than ten samples. The data range from a low of 0.04 mg/kg mercury from the Alamo River to a high of 0.98 mg/kg from the Guadalupe River.

The arithmetic mean and the median concentrations are similar in six out of seven cases, suggesting that the data may be normally distributed for these rivers. In many cases, sample sizes are great enough to test the distribution of the biota data for normality in individual water bodies. Although the mean and median values are similar for the Alamo River, the sample size for this water body is lower than for many of the others, so this should not be over-interpreted. In all cases, data for individual water bodies are not very variable (*e.g.*, the standard deviation is less than the mean). Additional collections in the rivers that lack samples and the Bear and Alamo rivers would lead to a more representative database for mercury in Trophic Level 4 organisms in California rivers. Since most of the water bodies have a similar mean concentration of mercury, it could be useful to collect enough data to determine whether bioaccumulation levels in the rivers with the lowest (Alamo and Bear rivers) and the highest (Guadalupe River) concentrations are really different from the other water bodies.

<sup>\*</sup> Number of samples collected

**Table 17.** Concentrations of methylmercury (mg/kg) in Trophic Level 4 biota<sup>+</sup>

Water Body	Arithmetic Mean	Standard Deviation	Median
Sacramento River (125)*	0.46	0.34	0.35
Mokelumne River (39)	0.69	0.37	0.69
Putah Creek (28)	0.38	0.19	0.34
San Joaquin River (261)	0.48	0.30	0.42
Napa River (0)	-	-	-
Bear River (15)	0.17	0.13	0.10
Coyote Creek (0)	-	-	-
Guadalupe River (41)	0.97	0.34	0.88
Alamo River (6)	0.04	0.02	0.04
Redwood Creek (0)	-	-	-

<sup>+</sup> Methylmercury was assumed to be 100 percent of total mercury in Trophic Level 4 biota

# 3.3.1.2 Water Data For Dissolved Methylmercury In Ten Rivers In California

The discussion that follows characterizes the dissolved methylmercury in the same ten California rivers where biota were collected. Table 18 summarizes the available dissolved methylmercury data for these rivers taken from the SWRCB California database. These mean dissolved methylmercury values for each river were derived from measured dissolved methylmercury and measurements of other forms of mercury that were converted into dissolved methylmercury. Overall, there was about three-fold greater number of converted values (223) compared to measured values (78). The total number of water samples collected (combined measured and converted) ranged from a high of 98 from the Bear River to a low of seven for the Alamo River. The standard deviations of the arithmetic means of these data were less than the means in six out of the ten rivers, indicating low variability for environmental data. The average mean value of dissolved methylmercury ranged from a low of 7.06x10<sup>-08</sup> mg/L for samples collected from Putah Creek to a high of 3.78x10<sup>-06</sup> mg/L for the Alamo River, a difference of slightly less than 200-fold. In eight out of ten cases, the mean and median were similar indicating that the data could be normally distributed, but statistical tests of normality were limited by the sample size. The mean and median were most dissimilar for the Guadalupe River, which had few samples, and the Bear River, which had the most samples. The source of these differences is not known.

For most water bodies, the mean dissolved methylmercury concentration was influenced by the greater number of converted values in the database. More measured dissolved methylmercury concentrations than converted concentrations were only available for the Mokelumne River and Putah Creek. Data from the Sacramento, San Joaquin and Bear rivers were selected to compare the concentration of measured vs. converted dissolved methylmercury. These rivers were selected because each had at least ten measured and ten converted values. When measured and converted concentration values in the Sacramento, San Joaquin and Bear rivers were compared (data not shown), the converted values were 2.3, 1.8, and 2.8-fold greater, respectively, than the

<sup>\*</sup> Number of samples collected

measured values. This indicates that using converted values can add two to three-fold to the concentration and perhaps contribute to greater variability and uncertainty in dissolved methylmercury concentrations. In order to reduce this variability and uncertainty, water samples of directly measured dissolved methylmercury should be collected in these water bodies, especially those with fewer measured values (Napa, Guadalupe, and Alamo rivers; and Coyote and Redwood creeks). Adding data for water bodies from other geographic areas of California would also improve the statewide coverage and representativeness of data for the lotic environment.

**Table 18.** Water dissolved methylmercury (DMeHg) concentrations for 10 rivers in California

	Sample	e Type <sup>+</sup>		DMeHg (mg/L)	
Location	Measured.	Converted	$\underline{Mean}^{\nabla}$	Standard Deviation	Median
Sacramento River (48)*	16	32	$9.00 \times 10^{-08}$	$8.52 \times 10^{-08}$	$7.14 \times 10^{-08}$
Mokelumne River (18)	16	2	$9.62 \times 10^{-08}$	$4.57 \times 10^{-08}$	$8.45 \times 10^{-08}$
Putah Creek (17)	15	2	$7.06 \times 10^{-08}$	$4.08 \times 10^{-08}$	$6.08 \times 10^{-08}$
San Joaquin River (40)	13	28	$8.06 \times 10^{-08}$	$4.51 \times 10^{-08}$	$7.20 \times 10^{-08}$
Napa River (21)	1	21	$2.66 \times 10^{-07}$	$2.20x^{-07}$	$1.93 \times 10^{-07}$
Bear River (98)	12	86	$3.51 \times 10^{-07}$	$9.53 \times 10^{-07}$	$8.70 \times 10^{-08}$
Coyote Creek (19)	2	17	$3.07 \times 10^{-07}$	$3.37 \times 10^{-07}$	$2.21 \times 10^{-07}$
Guadalupe River (9)	2	7	$2.54 \times 10^{-06}$	$3.97 \times 10^{-06}$	$8.79 \times 10^{-07}$
Alamo River (7)	0	7	$3.78 \times 10^{-06}$	$4.64 \times 10^{-14}$	$3.78 \times 10^{-06}$
Redwood Creek (22)	1	21	$9.09 \times 10^{-08}$	$7.00 \text{x} 10^{-08}$	$8.12 \times 10^{-08}$
Total	78	223			

<sup>+</sup> DMeHg measured (Meas.) or converted (Conv.) to DMeHg from total mercury or total methylmercury

These data are from the SWRCB database, March 2004.

Table 19 shows the BAFs for Trophic Level 2 biota calculated from dissolved methylmercury in biota and methylmercury in water from the SWRCB California database. Four of the rivers or creeks have biota methylmercury concentrations that allow the calculation of a BAF for this trophic level. The mean biota and water methylmercury concentrations are from all sites and all times of sampling. The BAFs range from high of  $2.01 \times 10^{+05}$  L/kg in the Sacramento River to a low of  $5.76 \times 10^{+04}$  L/kg in the Napa River. These individual BAFs differ by less than four-fold and the standard deviation of the overall mean  $(6.41 \times 10^{+04} \text{ L/kg})$  is less than the mean BAF of all water bodies combined  $(1.52 \times 10^{+05} \text{ L/kg})$ . It is clear from Table 19 that more data are necessary to attain a more representative database for Trophic Level 2 biota so that additional BAFs for this trophic level for more California water bodies can be calculated.

<sup>\*</sup> Total number of samples collected (sum of measured and converted)

Arithmetic mean of measured dissolved methylmercury concentrations and converted concentrations to dissolved methylmercury from total methylmercury or total mercury

**Table 19.** Concentrations of dissolved methylmercury in water, biota mercury concentrations and BAFs for Trophic Level 2

Water Body	Water DMeHg (mg/L)	Biota MeHg (mg/kg)	BAF (L/kg) <sup>+</sup>
Sacramento River (48,6)*	$9.00 \text{x} 10^{-08}$	0.018	$2.01 \times 10^{+05}$
Mokelumne River (18,0)	$9.62 \times 10^{-08}$	-	-
Putah Creek (17,5)	$7.06 \times 10^{-08}$	0.013	$1.78 \times 10^{+05}$
San Joaquin River (40,0)	$8.06 \text{x} 10^{-08}$	-	-
Napa River (21,11)	$2.66 \times 10^{-07}$	0.015	$5.76 \times 10^{+04}$
Bear River (98,0)	$3.51 \times 10^{-07}$	-	-
Coyote Creek (2,0)	$3.07 \times 10^{-07}$	-	-
Guadalupe River (9,0)	$2.54 \times 10^{-06}$	-	-
Alamo River (7,0)	$3.78 \times 10^{-06}$	-	-
Redwood Creek (22,9)	$9.09 \times 10^{-08}$	0.015	$1.70 \text{x} 10^{+05}$
		arithmetic mean	$1.52 \times 10^{+05}$
		Standard Deviation	$6.41 \times 10^{+04}$
* Number of samples (water	, biota)		
+ BAF = Biota MeHg (mg/k	g)/Water DMeHg (mg/L)		

Table 20 shows the BAFs for Trophic Level 3 biota calculated from dissolved methylmercury in biota and methylmercury in water from the SWRCB California database. It was not possible to develop a BAF for Redwood Creek because Trophic Level 3 biota were not collected from this water body. The BAFs range from a low of 1.59x10<sup>+04</sup> L/kg in the Alamo River to a high 3.82x10<sup>+06</sup> L/kg in the Sacramento River, which is a difference of about 240-fold. The standard deviation of the overall Trophic Level 3 BAF is again about as large as the mean itself  $(1.36 \times 10^{+06})$  and  $1.42 \times 10^{+06}$  L/kg, respectively), and is larger than the variation in biota or water concentrations. This variation could be due to the range of environments and biota with differing mercury levels used in these calculations. Although there are biota data for more water bodies for Trophic Level 3, as noted earlier, in many cases the biota results are based on fewer than ten samples (eight out of the ten rivers). Most of the samples in the current data set are from northern California rivers affected by mercury and gold mining. Collecting a larger database of biota samples from more lotic environments throughout the state could be useful to better characterize the range of bioaccumulation in this important trophic level that contains many fish that people catch and eat. If additional sampling takes place, it is suggested that collection of water and biota could be better coordinated to make the results more similar to the studies used by U.S. EPA in their development of BAFs.

**Table 20.** Concentrations of dissolved methylmercury in water, biota mercury concentrations and BAFs for Trophic Level 3

Water Body	Water DMeHg (mg/L)	Biota MeHg (mg/kg)	<b>BAF</b> (L/kg) <sup>+</sup>
Sacramento River (48,45)*	$9.00 \mathrm{x} 10^{-08}$	0.34	$3.82 \times 10^{+06}$
Mokelumne River 18,9)	$9.62 \times 10^{-08}$	0.31	$3.25 \times 10^{+06}$
Putah Creek (17,10)	$7.06 \text{x} 10^{-08}$	0.13	$1.82 \times 10^{+06}$
San Joaquin River (40,32)	$8.06 \text{x} 10^{-08}$	0.14	$1.70 \text{x} 10^{+06}$
Napa River (21,6)	$2.66 \times 10^{-07}$	0.26	$9.66 \times 10^{+05}$
Bear River (98,2)	$3.51 \times 10^{-07}$	0.21	$5.49 \times 10^{+05}$
Coyote Creek (19,5)	$3.07 \times 10^{-07}$	0.14	$4.50 \times 10^{+05}$
Guadalupe River (9,5)	$2.54 \times 10^{-06}$	0.53	$2.08 \times 10^{+05}$
Alamo River (7,5)	$3.78 \times 10^{-06}$	0.06	$1.59 \times 10^{+04}$
Redwood Creek (22,0)	$9.09 \times 10^{-08}$	-	-
		Arithmetic mean	$1.42 \times 10^{+06}$
		Standard deviation	$1.36 \text{x} 10^{+06}$
* Number of samples (war	ter, biota)		

Table 21 shows the BAFs for Trophic Level 4 biota calculated from dissolved methylmercury in biota and methylmercury in water from the SWRCB California database. BAFs for two of the water bodies, Napa River and Coyote Creek, could not be calculated because Trophic Level 4 biota were not collected. The BAFs range from a low of 1.06E<sup>+04</sup> L/kg in the Alamo River to a high of 7.14E<sup>+06</sup> L/kg in the Mokelumne River, which is a difference of about 670-fold. The overall mean and standard deviation for the BAFs for Trophic Level 4 biota in these rivers are 3.49E<sup>+06</sup> and 3.07E<sup>+06</sup> L/kg, respectively. Again there is more variation in bioaccumulation between water bodies than variation in the underlying biota and water concentrations. This variation is important to note because most of these water bodies have in common that they are in northern California in areas affected by past mercury and gold mining. Of course, there may be many environmental differences within this area, but if there is this much variation for similar water bodies, then the overall variation for a database that includes water bodies from southern California could be greater. Although the Trophic Level 4 dataset includes the highest sample sizes for biota, collecting a larger database of biota samples from more lotic environments throughout the state could be useful to better characterize the range of bioaccumulation in this important trophic level that typically shows the highest methylmercury bioaccumulation.

BAF = Biota Me Hg (mg/kg)/Water DMeHg (mg/L)

**Table 21.** Concentrations of dissolved methylmercury in water, biota mercury concentrations and BAFs for Trophic Level 4

Location	Water DMeHg (mg/L)	Biota MeHg (mg/kg)	$\mathbf{BAF} \left( \frac{L}{kg} \right)^{+}$
Sacramento River (48,125)*	$9.00 \text{x} 10^{-08}$	0.46	$5.10 \text{x} 10^{+06}$
Mokelumne River (18,39)	$9.62 \times 10^{-08}$	0.69	$7.14 \times 10^{+06}$
Putah Creek (17,28)	$7.06 \times 10^{-08}$	0.38	$5.36 \times 10^{+06}$
San Joaquin River (40,261)	$8.06 \times 10^{-08}$	0.48	$5.97 \times 10^{+06}$
Napa River (21,0)	$2.66 \times 10^{-07}$	-	-
Bear River (98,15)	$3.51 \times 10^{-07}$	0.17	$4.79 \times 10^{+05}$
Coyote Creek (19,0)	$3.07 \times 10^{-07}$	-	-
Guadalupe River (9,41)	$2.54 \times 10^{-06}$	0.97	$3.80 \times 10^{+05}$
Alamo River (7,6)	$3.78 \times 10^{-06}$	0.04	$1.06 \text{x} 10^{+04}$
Redwood Creek (22,0)	$9.09 \times 10^{-08}$	-	-
<b>,</b> , ,		Arithmetic mean	$3.49 \times 10^{+06}$
		Standard Deviation	$3.07 \times 10^{+06}$

<sup>\*</sup> Number of samples (water, biota)

Table 22 summarizes the BAFs for lotic environments in California calculated from the SWRCB California database using the alternative method. An unweighted arithmetic mean BAF was calculated for each trophic level from these data for the ten rivers. This is consistent with the U.S. EPA calculation, which also did not factor the number of replicates in a study into their calculations of mean BAFs. Some lotic environments have a larger dataset than others, so the BAF values from them are likely to be statistically more representative. The Bear River is an example of a dataset that is not very robust with respect to both water and biota data. In this river there were 98 water samples, and 0, 2 and 15 biota samples collected in Trophic Levels 2, 3 and 4, respectively. Other water bodies show similar data gaps especially for Trophic Level 2.

Table 22. Summary of bioaccumulation factors (BAFs) for lotic environments in California

2	3	4
	BAF (L/kg)	
$2.01 \times 10^{+05}$	$3.82 \times 10^{+06}$	$5.10 \text{x} 10^{+06}$
-	$3.25 \times 10^{+06}$	$7.14 \times 10^{+06}$
$1.78 \times 10^{+05}$	$1.82 \times 10^{+06}$	$5.36 \times 10^{+06}$
-	$1.70 \text{x} 10^{+06}$	$5.97 \times 10^{+06}$
$5.76 \times 10^{+04}$	$9.66 \times 10^{+05}$	-
-	$5.49 \times 10^{+05}$	$4.79 \times 10^{+05}$
-	$4.50 \times 10^{+05}$	-
-	$2.08 \times 10^{+05}$	$3.80 \times 10^{+05}$
-	$1.59 \times 10^{+04}$	$1.06 \text{x} 10^{+04}$
$1.70 \text{x} 10^{+05}$	-	-
$1.52 \times 10^{+05}$	$1.42 \times 10^{+06}$	$3.49 \times 10^{+06}$
		$3.07 \times 10^{+06}$
***************************************		
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These data are from the SWRCB database, March 2004.

<sup>+</sup> BAF = Biota MeHg (mg/kg)/Water DMeHg (mg/L)

The BAFs for the Trophic Levels 3 and 4 differ by slightly more than two-fold (1.42- $3.49 \times 10^{+06}$ ), but the difference between Trophic Level 2 and 3 is about 10-fold and between Trophic Level 2 and 4 about 20-fold. A pair-wise t-test (two-tail, unequal variance) was used to test whether the BAFs for these trophic levels were statistically different. The p-values are shown in Table 23. The BAFs for Trophic Levels 3 and 4 were not different (p=0.14), but the BAF for Trophic Level 2 was different than that for Trophic Level 3 (p=0.02) and Level 4 (p=0.03).

A similar pair-wise t-test comparison was performed for the U.S. EPA BAF data for the lotic environment. BAFs from U.S. EPA data were recalculated as arithmetic means for this statistical evaluation. The results of this evaluation are also shown in Table 23. Again, Trophic Level 3 and 4 BAFs are not statistically different, which might be expected since there are not consistent separations between all fish in these trophic levels. But Trophic Level 2 BAFs are different from both Trophic Level 3 and 4, showing the clearer separation between feeding behavior and bioaccumulation at these levels.

**Table 23**. Comparison of alternate California BAFs and recalculated arithmetic mean U.S. EPA BAFs among trophic levels for the lotic environment

	Trophic level (n)	Trophic level comparison	p statistic+
Alternate CA BAFs	(=	, , , , , , , , , , , , , , , , , , ,	F **********
$1.52 \times 10^{+05}$	2 (4)	2 vs. 3	0.02
$1.42 \times 10^{+06}$	3 (9)	2 vs. 4	0.03
$3.49 \times 10^{+06}$	4 (7)	3 vs 4	0.14
Recalculated* U.S.			
EPA BAFs			
$2.15 \times 10^{+05}$	2 (6)	2 vs. 3	0.02
$1.32 \times 10^{+06}$	3 (26)	2 vs. 4	0.05
$3.93 \times 10^{+06}$	4 (7)	3 vs 4	0.15
(n) = number of studies	s or water bodies include	ed to derive mean BAF	
*recalculated as arithm	etic means		
+ two-tail, unequal var	iance		

Alternate CA BAFs are from Table 22. U.S. EPA BAFs are recalculated from U.S. EPA (2000).

# 3.4 COMPARISON OF CALIFORNIA ALTERNATIVE BAFs AND U.S. EPA BAFS RECALCULATED AS ARITHMETIC MEANS FOR THE LOTIC ENVIRONMENT

The proceeding discussion demonstrated that California water body-specific BAFs could be derived from the SWRCB California database using an alternate methodology. A statistical comparison of the California and national BAFs was done in order to provide some basis for consideration of the difference between the alternatively calculated California BAFs and the U.S. EPA BAFs. Table 24 shows the results of a two tail pair-wise t-test of the mean California and

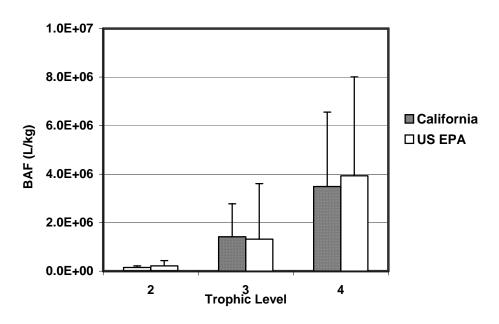
U.S. EPA BAF values for each trophic level. This statistical evaluation indicates that the mean BAFs for lotic environments from the U.S. EPA and California river-specific values do not differ (p>0.05) for any of the trophic levels. Figure 5 shows this overall similarity graphically.

Table 24. Statistical Evaluation of California and U.S. EPA BAFs for the Lotic Environment

Trophic Level	P Statistic*
2	0.34
3	0.89
4	0.82
* Two-tail test for unequal	variance

Data for comparisons are from Table 24.

Figure 5: California - U.S. EPA BAFs
Lotic Environment



Whiskers – standard deviation Plot of data from Table 23.

## 3.4.1 California Lentic Environment

It is not possible to calculate an alternative BAF for the lentic environment because only a single water body (Standish Dam) had any measurements of forms of mercury in water. As was

mentioned previously, biota were not collected for the analysis of mercury concentration from this water body. Consequently, the alternate method used to calculate BAFs for the lentic environment cannot be used with the data presently compiled in the SWRCB database. In contrast to the water data, there is a large dataset for mercury concentrations in biota in the lentic environment that could be used to calculate BAFs if corresponding water measurements were available.

## 3.4.2 California Estuarine Environment

The estuarine dataset in the SWRCB California database contains a sufficient number of fishwater combinations to enable recalculation of BAFs for this aquatic environment, but all data are from collection sites in the San Francisco Bay-Delta Estuary. The available biota and water data for the estuary are summarized below prior to calculating BAFs. Only data for Trophic Levels 2 and 4 are presently compiled in the SWRCB California database for this estuary.

Table 25 contains biota mercury concentrations for Trophic Level 2 biota collected from nine sites around San Francisco Bay. Most sites, with the exception of the South Bay, had Trophic Level 2 biota collected. Only four sites had ten or more samples collected. The mean values for methylmercury for this tropic level span a relatively narrow range from 0.010- 0.012 mg/kg. All of the standard deviations are less than the mean values. All of the medians are less than or equal to the mean values. This suggests that the data are normally distributed but the samples sizes are too small to adequately test the distribution. Additional biota samples should be collected to create a more representative database for this trophic level.

**Table 25.** Summary of methylmercury in Trophic Level 2 biota<sup>+</sup>collected from the San Francisco estuarine environment

<b>Location</b> (n <sub>b</sub> )*	Biota MeHg (mg/kg)					
	Mean	Standard Deviation	Median			
Alameda (10))	0.010	0.003	0.010			
Davis Pt (9)	0.012	0.004	0.012			
Dumbarton Bridge (10)	0.011	0.002	0.010			
Grizzly Bay (11)	0.011	0.004	0.010			
Pinole Pt (11)	0.011	0.003	0.011			
Red Rock (7)	0.012	0.002	0.013			
San Pablo Bay (8)	0.010	0.005	0.008			
South Bay (0)	-	-	-			
Yerba Buena (7)	0.012	0.002	0.011			

<sup>+</sup> Methylmercury was assumed to be 44 percent of total mercury in Trophic Level 2 biota

These data are from the SWRCB database, March 2004

Trophic Level 3 biota were not collected from the San Francisco Bay estuary so it will not be possible to summarize the data for these biota with respect to mercury concentrations nor to calculate a BAF.

<sup>\*</sup> Sample number of biota samples collected

Summary information on Trophic Level 4 biota collected for mercury analyses are presented in Table 26. The SWRCB California database contained only four collections of Trophic Level 4 biota. Two of these collections contained ten or fewer samples, but larger sample sizes were available at two sites, San Pablo Bay (n=47) and South Bay (n=48). The mercury concentrations in these biota ranged from a low of 0.12 mg/kg at the Dumbarton Bridge to a high of 0.60 mg/kg at South Bay, a difference of five-fold. The standard deviations were less than the means, and the medians were similar to the means for collections with few samples. However, for the two collections with a larger sample size, the means and medians were more dissimilar. In order to achieve a more representative estimate of the mercury levels and BAFs for this tropic level, additional sampling should be considered.

**Table 26.** Summary of methylmercury in Trophic Level 4 biota<sup>+</sup> collected from the San Francisco estuarine environment

<b>Location</b> (n <sub>b</sub> )*	Biota MeHg (mg/kg)				
	<u>Mean</u>	<b>Standard Deviation</b>	<u>Median</u>		
Alameda (0)	-	-	-		
Davis Pt (10)	0.55	0.17	0.50		
Dumbarton Bridge (3)	0.12	0.047	0.11		
Grizzly Bay (0)	-	-	-		
Pinole Pt (0)	-	-	=		
Red Rock (0)	-	-	-		
San Pablo Bay (47)	0.39	0.28	0.28		
South Bay (48)	0.60	0.40	0.40		
Yerba Buena (0)	-	-	-		

<sup>+</sup> Methylmercury was assumed to be 100 percent of total mercury in Trophic Level 4 biota

These data are from the SWRCB database, March 2004

Table 27 summarizes water data for measured and converted dissolved methylmercury for the San Francisco Bay estuarine environment. The mean values are averaged over all times that a site was monitored and may include both measured and converted values. Measured values were only available for four sites and, in these cases, only one or two measured samples were taken. Out of 185 water samples only eight (<5 percent) were for directly measured dissolved methylmercury concentration. In contrast, for the lotic environment, nearly 25 percent of water values were directly measured dissolved methylmercury. A comparison of the measured and converted values in the estuarine environment suggests that this reliance on converting other measurements to dissolved methylmercury may have biased these results. The mean concentration based on measured and converted dissolved methylmercury was 2.37x10<sup>-06</sup> mg/L, but the mean concentration based on measured dissolved methylmercury only was 4.99x10<sup>-08</sup> mg/L. This is about a 500-fold difference. Other reported concentrations for directly measured dissolved methylmercury in water from San Francisco Bay in the literature are more similar to the limited number of measured values in the SWRCB California database. The mean concentration from Conaway *et al.* (2003) was 4.47x10<sup>-08</sup> mg/L and that from California Regional Water Quality Control Board (2000) was 3.21x10<sup>-08</sup> mg/L.

<sup>\*</sup> Sample size of biota collected.

The converted values for the estuarine environment based on the SWRCB California database will be discussed here and used to calculate BAFs. However, it should be noted that using just the measure concentrations of dissolved methylmercury might yield different results. And it would be important to collect additional data for measured dissolved methylmercury in the San Francisco estuary.

Nine sites had sample sizes of 17 or more in the SWRCB California database with converted water concentrations for dissolved methylmercury. The values for mean dissolved methylmercury (combining measured and converted concentrations) range from a low of  $5.51 \times 10^{-07} \text{mg/L}$  at Yerba Buena to a high of  $3.75 \times 10^{-06} \text{ mg/L}$  at San Pablo Bay, which is a difference of about seven-fold. In three of the nine locations, Davis Point, Dumbarton Bridge and San Pablo Bay, the standard deviation exceeded the mean suggesting that, at these sites, the data were somewhat more variable than at the other six sites. The reason for this is unknown. The overall mean dissolved methylmercury concentration was  $2.37 \times 10^{-06} \text{ mg/L}$ .

**Table 27.** Summary of water dissolved methylmercury (DMeHg) concentration for locations in the San Francisco Estuary

	Water S	amples:		DMeHg (mg/L)	
Location (n*)	Meas.	Conv.	Mean <sup>+</sup>	Standard Deviation	<u>Median</u>
Alameda (20)	2	18	$5.59 \times 10^{-07}$	$3.95 \times 10^{-07}$	$4.66 \times 10^{-07}$
Davis Pt (21)	2	19	$3.31 \times 10^{-06}$	$3.70 \times 10^{-06}$	$2.17x10^{-06}$
Dumbarton Bridge (20)	0	20	$3.32 \times 10^{-06}$	$3.45 \times 10^{-06}$	$1.87 \times 10^{-06}$
Grizzly Bay (23)	2	21	$3.72 \times 10^{-06}$	$3.54 \times 10^{-06}$	$2.45 \times 10^{-06}$
Pinole Pt (20)	0	20	$2.34 \times 10^{-06}$	$2.26 \times 10^{-06}$	$5.06 \times 10^{-06}$
Red Rock (18)	1	17	$9.43 \times 10^{-07}$	$6.57 \times 10^{-07}$	$8.36 \times 10^{-07}$
San Pablo Bay (22)	0	22	$3.75 \times 10^{-06}$	$4.39 \times 10^{-06}$	$1.52 \times 10^{-06}$
South Bay (20)	0	20	$2.83 \times 10^{-06}$	$2.04 \times 10^{-06}$	$2.47 \times 10^{-06}$
Yerba Buena (22)	1	21	$5.51 \times 10^{-07}$	$3.24 \times 10^{-06}$	$5.61 \times 10^{-07}$
Sum	8	178			
	Arith	metic mean	$2.37 \times 10^{-06}$		

<sup>\*</sup> Total number of samples (Measured + Converted)

These data are from the SWRCB database, March 2004

The BAFs calculated from the biota data in Tables 25 and 26, and the dissolved methylmercury data in Table 27, are shown in Table 28. The BAFs for Trophic Level 2 range from  $2.43 \times 10^{+03}$  L/kg at San Pablo Bay to a high of  $1.85 \times 10^{+04}$  L/kg at Alameda, a difference of about eight-fold. The arithmetic mean value for Trophic Level 2 is  $8.71 \times 10^{+03}$  L/kg. The standard deviation  $(7.67 \times 10^{+03})$  is slightly less than the mean. The BAFs for Trophic Level 4 ranged from a low of  $3.73 \times 10^{+04}$  L/kg at Dumbarton Bridge to a high of  $2.11 \times 10^{+05}$  a South Bay, a difference of about six-fold. The arithmetic mean value for Trophic Level 4 is  $1.3 \times 10^{+05}$  L/kg and the standard deviation  $(7.64 \times 10^{+04})$  is slightly less than the mean. The BAF for Trophic Level 4 is about 15-fold greater than the Trophic Level 2 BAF. Statistical evaluation of these data using a two-tailed t-test with unequal variance shows that they were of borderline significance (p = 0.051). BAFs recalculated using just directly measured dissolved methylmercury (to improve data quality) are

<sup>+</sup> Arithmetic mean of measured DMeHg and converted (DMeHg from THg and DMeHg from TMeHg)

also show in Table 28. Additional biota, especially Trophic Level 3 and 4, and water samples, especially measured dissolved methylmercury, should be considered for future collections in San Francisco Bay and other California estuarine environments. This would yield a more representative database of values. If additional biota and water sampling were to occur, it would be best to coordinate water and biota sampling to increase similarity with the methodology used by U.S. EPA.

Table 28. Summary BAFs for the Estuarine Environment

		Biota MeH	g (mg/kg)	BAF(I	_/kg) <sup>+</sup>
Location(n*)	Water (mg/L)	<u>TL 2</u>	<u>TL 4</u>	<u>TL 2</u>	<u>TL 4</u>
Alameda (20; 10,0)	$5.59 \times 10^{-07}$	0.010	-	$1.85 \times 10^{+04}$	-
Davis Pt (21; 9, 10)	$3.31 \times 10^{-06}$	0.012	0.55	$3.37 \times 10^{+03}$	$1.70 \text{x} 10^{+05}$
Dumbarton Bridge (20; 10,3)	$3.32 \times 10^{-06}$	0.011	0.12	$3.30 \text{x} 10^{+03}$	$3.73 \times 10^{+04}$
Grizzly Bay (23; 11, 0)	$3.72 \times 10^{-06}$	0.011	-	$3.00 \text{x} 10^{+03}$	-
Pinole Pt (20; 11, 0)	$2.34 \times 10^{-06}$	0.011	-	$4.70 \text{x} 10^{+03}$	-
Red Rock (18; 7, 0)	$9.43 \times 10^{-07}$	0.012	-	$1.30 \text{x} 10^{+04}$	-
San Pablo Bay (22; 8, 47)	$3.75 \times 10^{-06}$	0.010	0.39	$2.43 \times 10^{+03}$	$1.05 \text{x} 10^{+05}$
South Bay (20; 48, 48)	$2.83 \times 10^{-06}$	-	0.60	-	$2.11x10^{+05}$
Yerba Buena (22; 7, 0)	$5.51 \times 10^{-07}$	0.012	-	$2.13x10^{+04}$	-
		Unweighted Ari	thmetic Mean	$8.71 \times 10^{+03}$	$1.30 \times 10^{+05}$
		Stand	lard Deviation	$7.67 \times 10^{+03}$	$7.64 \times 10^{+04}$
Values recalculated using just	mercurv.	$2.2 \times 10^{+5}$	$8.3x10^{+6}$		
* Sample sizes of water; biota collected (Trophic Level 2, 4)					
+ BAF = Biota (mg/kg)/Wate	` •				

These data are from the SWRCB database, March 2004

# 3.5 COMPARISON OF U.S. EPA AND CALIFORNIA TRANSLATORS

The discussion that follows compares translators derived from the SWRCB California database to the U.S. EPA translators. Only lotic translators can be directly compared because these were the only translators for which national and California data were available. Both sets of lotic translators are shown in Table 29. U.S. EPA used multiple studies that met specific analytical criteria to derive national translators. Like the studies used by U.S. EPA for BAFs, many of these studies contained replicates, so the number of U.S. EPA studies in Table 29 are not directly comparable to the number of entries from the SWRCB California database. The major difference between the U.S. EPA translators is that they came from individual studies by the same investigators, whereas, in order to calculate translators from the SWRCB California database, data from different investigators for the same water bodies were used. U.S. EPA translators have been recalculated as arithmetic means to allow comparison with the SWRCB California database translators. The differences and similarities between the U.S. EPA and translators calculated using the data compiled by SAIC in the SWRCB database will be discussed for each translator.

#### 3.5.1 Lotic Environment

Table 29 shows the translators for lotic environment derived from the SWRCB California database and the translators from U.S. EPA for this aquatic environment.

**Table 29.** Translators for the Lotic Environment: California and U.S. EPA

Source	Translator:	DHg/THg		
	n*	Mean (Star	ndard Deviation)	Range
California	117	0.31	(0.86)	0.01-6.88
U.S. EPA	19	0.44	(0.24)	0.10-0.90
			DMeH	Ig/THg
California	37	0.015	(0.012)	0.003-0.042
U.S. EPA	13	0.020	(0.016)	0.002-0.051
			DMeHg/T	МеНд
California	46	0.51	(0.26)	0.04-1.04
U.S. EPA	13	0.53	(0.20)	0.17-0.83

<sup>\*</sup> Number of samples (U.S. EPA number of studies; California number of entries in the SWRCB database)
These data are from the SWRCB database, March 2004

# 3.5.1.1 Translator for DHg/THg

The arithmetic mean value for DHg/THg from U.S. EPA (0.44) is higher than the value of 0.31 derived from the SWRCB California database. The California data range is 0.01-6.88 compared to the U.S. EPA's data range of 0.10-0.90. The standard deviations for the U.S. EPA and California arithmetic means are and 0.24 and 0.86, respectively. The U.S. EPA, through its quality assurance and quality control, did not include studies that reported ratios of DHg/THg that were greater than one (unity) as it is not possible for the concentration of dissolved mercury to exceed the concentration of total mercury. Therefore, the range of values in the California dataset is unreasonable and includes some analytically invalid data. These invalid data can be eliminated by censoring (i.e., deleting) any data with a ratio greater than one when calculating a translator mean. When values greater than one are removed from the DHg/THg SWRCB California dataset, the arithmetic mean becomes 0.18, which is 2.4-fold below the arithmetic mean for the U.S. EPA dataset. One reason for the lower mean value for this translator in California compared to the U.S. EPA value may be related to the absence of data less than 0.10 in the U.S. EPA dataset. In the California dataset, 28 percent of values for the ratio DHg/THg range from 0.01-0.09. This may indicate some unique environmental conditions in California lotic environments or additional problems with data quality. Statistical evaluation of the U.S. EPA and California arithmetic mean values using a two-tail t-test with unequal variance indicates that they are not different (p = 0.17).

# 3.5.1.2 Translator for DMeHg/THg

The arithmetic mean value for DMeHg/THg for U.S. EPA's translator (0.020) is higher than the value (0.015) derived from the SWRCB California dataset. The range of the values for the U.S. EPA dataset is 0.002-0.051 and the range for the California dataset is 0.003-0.042. The standard deviations for the U.S. EPA and California arithmetic means are 0.016 and 0.012, respectively. In both cases, the standard deviation is lower than but similar to the mean. Statistical evaluation of U.S. EPA and California arithmetic mean values using a two-tail t-test for unequal variance indicates that they are not different (p = 0.29). Given the similarity of the means for the data from California and U.S. EPA and the observation that the dataset from California contains a reasonable range of values (none greater than one), either translator would yield a similar value when converting a total mercury concentration into a dissolved methylmercury concentration.

# 3.5.1.3 Translator for DMeHg/TMeHg

The arithmetic mean values for this translator from U.S. EPA and SWRCB California datasets are 0.53 and 0.51, respectively. The data ranges for U.S. EPA and California are 0.17-0.83 and 0.04-1.04, respectively. The minimum values from the SWRCB California dataset are approximately four-fold lower (0.04 vs. 0.17) than the U.S. EPA dataset. The standard deviations for these data are 0.20 (U.S. EPA) and 0.26 (California). Also, there are two values in the California dataset that exceed one, suggesting that the quality of the SWRCB California dataset should be examined. Comparison of the U.S. EPA and California mean values with a two-tail t-test for unequal variance indicates that they are not different (p = 0.70). When the two data points in the dataset for DMeHg/TMeHg with values greater then one are removed, then the mean value for this translator becomes of 0.49, which is an insignificant change in this relationship. After censoring the values above one in the SWRCB California dataset, there is no clear reason to recommend either the California or U.S. EPA translator for TMeHg to DMeHg.

#### 3.5.2 Lentic Environment

It is not possible to derive translators for the lentic environment because only data for one water body, Standish Dam, are compiled in the SWRCB California database. Other data exist for the lentic environment in, for example, Clear Lake and Lake Berryessa, but they were not included in the SWRCB California database as currently evaluated. If adequate values for concentrations of all forms of mercury in water in lentic environments can be compiled from other sites in California, then it may be possible to calculate these translators.

## 3.5.3 Estuarine Environment

# 3.5.3.1 Translator for DHg/THg

Sufficient data exist for derivation of a translator for DHg/THg in the estuarine environment. Table 30 summarizes these data for eight sites in the San Francisco Bay-Delta Estuary. This table contains the arithmetic mean and standard deviations for data from these sites within San Francisco Bay. The number of water samples available to calculate this translator range from a high of 19 in Grizzly Bay to a low of 12 in Alameda. The translators ranged from a low of 0.12 in two locations, Davis Point and Grizzly Bay, to a high of 0.30 in Alameda. The arithmetic

mean for these data is 0.15. The U.S. EPA reports a geometric mean translator value of 0.35 for DHg/THg in the estuarine environment. The raw U.S. EPA data for this translator are not readily available so it was not possible to recalculate the U.S. EPA value as an arithmetic mean to compare it statistically with the California-based translator.

**Table 30.** Translator (DHg/THg) for sites in San Francisco Bay

Site (n)*	Arithmetic Mean	Standard Deviation
Alameda (12)	0.30	0.15
Davis Point (16)	0.12	0.12
Dumbarton Bridge (18)	0.16	0.11
Grizzly Bay (19)	0.12	0.09
Pinole Point (16)	0.14	0.11
Red Rock (15)	0.23	0.14
San Pablo Bay (15)	0.13	0.10
South Bay (18)	0.15	0.10
Arithmetic Mean	0.15	
n Number of samples		

These data are from the SWRCB database, March 2004

Comparison of these data using a pair-wise t-test for unequal variance showed that mean values for Alameda and Grizzly Bay or Davis Point (the two extremes of the dataset) are different (p=0.0012), while the mean values for Alameda and Red Rock are not different (p=0.22). The mean values of Alameda and Dumbarton are different (p=0.009), while the mean values for Red Rock and Dumbarton are not different (p=0.11). Therefore, the translator for Alameda is statistically greater than all other sites except for Red Rock. This can be seen graphically in Figure 6, which displays the translator mean at each site in the San Francisco Bay along with the standard deviations (whiskers) of the mean for each site. The reason for this difference at Alameda is not known.

San Francisco Bay: DHg/THg

0.50

0.40

0.30

0.20

0.10

0.00

Davis Point

Davis Point

Pinole Point

Crittin Davis Point

Crittin Davis Point

Da

Figure 6. DHg/THg at several sites in the San Francisco Bay

The data plotted in this figure are from the SWRCB database, March 2004, as shown in Table 30.

A San Francisco Estuary-wide translator of 0.15 for DHg/THg can be derived using data from all of the sampling sites. Even though it has been demonstrated that statistical differences exist between sites, it is consistent with the U.S. EPA translator approach to derive an estuary-wide translator. U.S. EPA combined data over broader geographic areas (*e.g.*, the United States, Europe and Siberia) than San Francisco Bay without regard to potential differences between sites for the derivation of BAFs and translators. Regardless, this California translator is of limited use because it does not yield a translator to dissolved methylmercury.

# 3.5.3.2 Translator for DMeHg/THg

It is not possible to develop a California-specific translator for DMeHg/THg in the estuarine environment because only eight values of measured dissolved methylmercury (DMeHg) are compiled in the SWRCB California database. Also, when DMeHg was measured, no corresponding values for THg were measured.

# 3.5.3.3 Translator for DMeHg/TMeHg

There are less than ten entries in the SWRCB California dataset that could be used to develop an estuarine California-specific translator for DMeHg/TMeHg. Further, the data quality in these measurements was poor, as dissolved mercury forms sometimes exceeded total mercury. Additional data could be collected to so that this translator can be derived.

# 3.6 CONCLUSIONS CONCERNING DERIVING BAFs AND TRANSLATORS FROM THE SWRCB CALIFORNIA DATABASE

# 3.6.1 Conclusions concerning California BAFs

OEHHA found a number of differences between the database and methodology used by SAIC to derive BAFs and the U.S. EPA database and methodology. Both databases used the best quality data that could be identified at the time but the U.S. EPA criteria could be more stringent due to its broader geographic scope. Some specific instances were noted in the discussion above where the values in the SWRCB database were unrealistic. Some of these problems can be overcome by censoring such data. Also, OEHHA found that, while the U.S. EPA based individual BAF calculations on water and biota data collected and measured in the same study, the water and biota data compiled in the SWRCB California database, even when collected from the same water body, were from different studies. This potentially increases data variability due to different analytical techniques and quality control measures between study researchers. Coordinating biota and water sampling in California and standardizing analytical techniques and quality control measures would help to reduce variability for future data added to this database. OEHHA also found that the method SAIC used to calculate BAFs was different than that used by U.S. EPA.

Despite these differences, OEHHA demonstrated that California-specific BAFs could be calculated using the data in the SWRCB California database by an alternative method for lotic and estuarine environments. This alternate method is very similar to the U.S. EPA method. OEHHA calculated arithmetic mean values for the alternate California-specific BAFs. U.S. EPA's national BAFs were calculated as geometric means. The U.S. EPA and California-specific BAFs are shown in Table 31. OEHHA used arithmetic means because they are more health protective and because in most cases the sample size for data for individual water bodies was insufficient to determine the form of the distribution. The alternate California-specific BAFs calculated by OEHHA were shown to be similar to U.S. EPA's BAFs, especially U.S. EPA values recalculated as arithmetic means. The alternate California-specific BAFs calculated by OEHHA and the U.S. EPA BAFs re-calculated as arithmetic means were not statistically different. This suggests that the current SWRCB California database can be used to calculate some California-specific BAFs. OEHHA also calculated estuarine BAFs although U.S. EPA could not. These BAFs when calculated using only directly measured methylmercury in water (to improve data quality) are also similar to the national default values (see values in Table 31).

OEHHA found "gaps" in the available data for the SWRCB California database that limited the aquatic environments and trophic levels for which California-specific BAFs could be calculated. Filling these data gaps could improve the application of the database. The following are some of the consequences of these gaps in data availablility:

■ California-specific BAFs could not be calculated for any trophic level in lentic environments due to insufficient data. Biota data were available for one water body, but there were no corresponding water data. Water data and additional corresponding biota

data are needed from lentic water bodies throughout California in order to calculate California-specific BAFs for the lentic environment.

- A combined lentic/lotic California-specific BAF equivalent to the U.S. EPA national BAF cannot be calculated because of the lack of lentic data for California.
- California-specific BAFs could not be calculated for Trophic Level 3 in the estuarine environments due to insufficient data. Trophic Level 3 biota data are needed from San Francisco Bay in order to calculate California-specific BAFs for Trophic Level 3 in this estuarine environment. Data for dissolved methylmercury measured in water and mercury measurements in Trophic Level 2, 3, and 4 biota in other estuarine water bodies in California would also useful to develop estuarine BAFs representative of a range of California estuaries. However, a complete dataset for San Francisco Bay is especially important because of the size and importance of this water body.
- OEHHA found that the sample size for biota and water data entered into the SWRCB California database was often low. BAFs based on more samples will be more accurate than those based on fewer samples. Larger samples sizes of water and biota data are needed from water bodies throughout California in order to calculate more accurate California-specific BAFs.
- OEHHA found that the geographic range of lotic, lentic, and estuarine water bodies in California compiled in the SWRCB California database was very limited. The available water bodies are not representative of the range of California environmental conditions. Data for the lotic environment was primarily from northern California and the Sacramento-San Joaquin River watersheds. Data for the estuarine environment were exclusively from the San Francisco Bay-Delta estuary. Both of these areas are heavily impacted by runoff and deposition from mercury and gold mining. Data from Standish Dam were the only data for the lentic environment in the SWRCB California database. Additional water and biota data (for all trophic levels) are needed from water bodies throughout California in order to calculate California-specific BAFs that are representative of a range of California water bodies.

SWRCB should attempt to fill these data gaps to develop a complete spectrum of California-specific BAFs for each trophic level in lentic, lotic, and estuarine environments. Some additional new data may be available in recent literature. For example, several new studies for the San Francisco Bay Estuary are available in which multiple forms of mercury in water have been measured (Conway, *et al.*, 2003; Choe *et al.*, 2003a; b). Data from these and other studies that may become available in the future could be added to the SWRCB California database.

Based on these comparisons there is not a clear-cut scientific basis that shows that either the national or California-specific BAFs will yield more accurate results if used in a methylmercury implementation policy. California-specific BAFs calculated as arithmetic means will yield higher tissue concentrations in biota at a given concentration of dissolved methylmercury in water. Consequently, allowable water concentrations based on the OEHHA alternate California-

specific BAFs would be lower than those based on the geometric mean U.S. EPA BAFs. Thus, the California-specific BAFs will be more health protective, but could not be developed for all environments and trophic levels. U.S. EPA BAFs could be used for environments and trophic levels where California-specific BAFs are not available. In order to determine if the California-specific or U.S. EPA BAFs would work best in the methylmercury implementation policy they should be tested to see how well they predict biota tissue concentrations at different trophic levels based on water data for various water bodies in California. This is a necessary step in validating both the U.S. EPA and California-specific BAFs and determining their limitations in a practical application. This testing could also show which BAFs would be more applicable in California or help find environmental conditions for which default BAFs do not work.

Table 31: Summary of Bioaccumulation Factors (BAFs) from the U.S. EPA and California data

			Trophic Level		
Agency	Environment/Comments	Mean	<u>2</u>	<u>3</u>	<u>4</u>
U.S. EPA	Lentic/Lotic Combined	Geometric	$1.2x10^{+05}$	$6.8 \times 10^{+05}$	$2.7x10^{+06}$
U.S. EPA	Lentic/Lotic Combined	Arithmetic	$1.9 \times 10^{+05} *$	$1.4 \times 10^{+06} *$	$5.0 \text{x} 10^{+06} \text{*}$
California	Lentic/Lotic Combined	Geometric	NP	NP	NP
	Alternative				
California	Lentic/Lotic Combined	Arithmetic	NP	NP	NP
	Alternative				
California	Lentic/Lotic Combined	Arithmetic	ND	ND	ND
	SAIC calculated				
U.S. EPA	Lentic Only	Geometric	$1.3 \text{x} 10^{+05}$	$1.1x10^{+06}$	$5.7x10^{+06}$
U.S. EPA	Lentic Only	Arithmetic	$1.6 \times 10^{+05} *$	1.5	$6.2 \times 10^{+06} * !!$
	•			x10 <sup>+06</sup> *!!	
California	Lentic Alternative	Geometric	NP	NP	NP
California	Lentic Alternative	Arithmetic	NP	NP	NP
California	Lentic SAIC calculated	Arithmetic	$1.3x10^{+04}$	$5.5 \times 10^{+05}$	$7.3x10^{+05}$
H.C. ED.	1 0.1	G	1.1.10+05	<b>5.7.</b> 10±05	1.2.10+06
U.S. EPA	Lotic Only	Geometric	$1.1 \times 10^{+05}$	$5.7 \times 10^{+05}$	$1.2 \times 10^{+06}$
U.S. EPA	Lotic Only	Arithmetic	$2.1 \times 10^{+0.5} *$	$1.3 \times 10^{+06} *$	$3.9 \times 10^{+06} *$
California	Lotic Alternative	Geometric	$4.2 \times 10^{+0.5}$	$6.8 \times 10^{+0.5}$	$1.1 \times 10^{+06}$
California	Lotic Alternative	Arithmetic	$1.2 \times 10^{+06} *!!$	$1.4 \times 10^{+06} *$	$3.5 \times 10^{+06}$
California	Lotic SAIC calculated	Arithmetic	2.3x10 <sup>+04</sup>	$5.8 \times 10^{+05}$	$7.4 \text{x} 10^{+05}$
U.S. EPA	Estuarine	Geometric	NP	NP	NP
U.S. EPA	Estuarine	Arithmetic	NP	NP	NP
California	Estuarine Alternative	Geometric	$6.1 \times 10^{+03}$	NP	$1.1 \times 10^{+05}$
California	Estuarine Alternative	Arithmetic	$8.7 \times 10^{+03} *$	NP	$1.3 \times 10^{+05} *$
California	Estuarine Alternative	Arithmetic	2.45x10 <sup>+05</sup> #	NP	8.3x10 <sup>+06</sup> #
California	Estuarine SAIC calculated	Arithmetic	$6.3 \times 10^{+03}$	$5.6 \times 10^{+04}$	$2.2 \times 10^{+05}$

NP: Not possible to calculate from current California or national database.

These values were calculated using U.S. EPA estuarine translators. This was necessary because the SWRCB database did not contain data needed to calculate a total mercury to dissolved methylmercury translator.

# 3.6.2 Conclusions Concerning California Translators

Translators were not originally calculated from the California data compiled in the SWRCB California database. However, OEHHA determined that, in some cases, there were data in the database that could be used to calculate California-specific translators using the same method used to calculate California-specific BAFs. Just as California-specific BAFs might be more representative of California environments than national BAFs, California-specific translators

ND: Not done.

<sup>\*</sup>Maximum BAF for this trophic level and this water body environment.

<sup>!!</sup>Maximum BAF for this trophic level

<sup>#</sup> These values were calculated using directly measured dissolved methylmercury concentrations from a limited number of measurements from the San Francisco estuary in the SWRCB database, March 2004.

might work better to convert water data from California into dissolved methylmercury for calculating California-specific BAFs. OEHHA calculated translators from data in the database. These are shown with U.S. EPA translators in Table 32. These translators are subject to the same data quality limitations as the California-specific BAFs.

Translators are very important because they are often necessary to convert the form of mercury measured in water into dissolved methylmercury, the form needed to calculate BAFs. U.S. EPA derived three different translators for each aquatic environment (lentic, lotic, and estuarine): a translator between measured total mercury and dissolved total mercury (DHg/THg); a translator between measured total mercury and dissolved methylmercury (DMeHg/THg); and a translator between measured total methylmercury and dissolved methylmercury (DMeHg/TmeHg).

OEHHA found "gaps" in the data available for the SWRCB California database that limited which California-specific translators could be calculated. No California-specific translators could be calculated for lentic environments due to insufficient data. Water data are for all forms of mercury in water from lentic water bodies throughout California would be needed in order to calculate California-specific translators for the lentic environment. The only California-specific translator that could be calculated for the estuarine environments was DHg/THg. Data were insufficient to calculate other translators for this environment. The samples sizes for these calculations were small and the geographic range of water bodies in California was limited. It is possible to develop estuarine translators for DMeHg/THg and DMeHg/TMeHg from California-specific data from published studies in the literature (Conway *et al.*, 2003; Choe, *et al.* 2003a,b).

It was possible to calculate all three translators for lotic environments from the SWRCB database. All of these California-specific translators were similar to the corresponding U.S. EPA translator. The California and U.S. EPA translators were not statistically different. The samples sizes for these calculations were reasonable (all above 35 samples) but the geographic range of water bodies in California was limited. The limited geographic range of lotic, lentic, and estuarine water bodies compiled in the SWRCB California database (as discussed for BAFs) could also affect the California-specific translators. Additional data for all forms of mercury in water are needed from water bodies throughout California in order to calculate more representative California-specific translators.

There is no clear-cut scientific basis that shows that either the national or California-specific translators will yield more accurate results if used in a methylmercury implementation policy. The U.S. EPA data quality might be better but this cannot be proven and censoring some California data improves the overall SWRCB database quality. The chief reason to use the California-specific translators is that they may be more representative of California environmental conditions. But a significant problem is that appropriate translators could not be calculated in all environments due to a lack of data. SWRCB should also attempt to fill translator data gaps.

Table 32: Summary of Translators: comparison of U.S. EPA and California-based translators

Translator (f <sub>d</sub> )	Data Source	Statistic	Lentic	Lotic	Estuarine
f <sub>d</sub> Hg	U.S. EPA*	Geometric	0.60	0.37	0.35
	U.S. EPA	Arithmetic	NC	0.44	CR
	California	Arithmetic	ND	0.31	0.15
f <sub>d</sub> MeHg <sub>d</sub> /MeHg <sub>t</sub>	U.S. EPA	Geometric	0.032	0.014	0.19
	U.S. EPA	Arithmetic	NC	0.020	NC
	California	Arithmetic	ND	0.015	ND
f <sub>d</sub> MeHg <sub>d</sub> /MeHg <sub>t</sub>	U.S. EPA	Geometric	0.61	0.49	0.61
	U.S. EPA	Arithmetic	NC	0.53	NC
	California	Arithmetic	ND	0.51	ND

ND Data do not exist in the SWRCB database

NC Not calculated: because comparison of U.S. EPA data not possible because California data do not exist.

CR OEHHA cannot reproduce U.S. EPA's geometric mean value of 0.35 for this translator. Therefore, OEHHA is unsure that we have all of the data used by U.S. EPA and have not attempted to recalculate the arithmetic mean.

U.S. EPA values are from Table 9 and U.S. EPA (2000). California translators are calculated from the SWRCB database, March 2000. See Table 29 and 30 and text.

# 4 TESTING PREDICTIONS OF BIOTA MERCURY CONCENTRATIONS FROM DISSOLVED METHYLMERCURY CONCENTRATIONS IN WATER USING BIOACCUMULATION FACTORS

U.S. EPA calculated national default BAFs but did not evaluate their practical application by using them to predict fish tissue methylmercury concentrations from measured dissolved methylmercury concentrations in water. Predictions using default BAFs and translators should be tested for accuracy for multiple water bodies to evaluate their potential strengths, weaknesses and limitations. Water and tissue mercury concentrations from water bodies in the California SWRCB database compiled by SAIC will be used to test the U.S. EPA national default BAFs. Ten California lotic water bodies were selected for this testing. These water bodies were selected because data for dissolved methylmercury in water (converted and/or directly measured) and methylmercury in biota from one or more trophic levels were available from each of them for one or more trophic levels. It was not possible to perform a comparable test for lentic water bodies and BAFs due to gaps in available California data. Water and tissue measurements from all "sites" and times within each water body were used to derive a single water and tissue arithmetic mean value for that water body in this prediction exercise. Biota tissue levels for all trophic levels with BAFs (Trophic Levels 2, 3, and 4) were only available for the Sacramento River and Putah Creek. All ten lotic water bodies and their mean dissolved methylmercury levels are shown in Table 33, 34, and 35. Table 33 shows the predicted biota methylmercury level for Trophic Level 2 in all water bodies, and the actual arithmetic mean measured level, where available. Table 34 shows predicted and actual measured methylmercury levels for Trophic Level 3 from these water bodies, and Table 35 does the same for Trophic Level 4. The predicted values were derived by multiplying arithmetic mean BAFs derived from the U.S. EPA data (see discussion in the prior section) by the arithmetic mean of water concentrations of dissolved methylmercury (converted and/or directly measured) in each river.

Accompanying each table is a figure that plots the predicted and actual measured biota values for the subset of water bodies that have actual measured biota values for one trophic level at a time. Figures 7, 8, and 9 show plots corresponding to the respective trophic levels in Tables 33, 34, and 35. In each figure, some predicted values are close to the measured values. The predicted values closest to their respective measured values are indicated within a dashed circle. The drawing of the dashed circles or ovals in figures is not based on quantitative characterization of a mathematically defined cluster, but is qualitative and intended to call the reader's attention to the observation that, for the water bodies represented by the points within the dashed lines, the BAFs yielded a reasonable prediction of the actual values. Matched water and biota sampling using larger sample sizes are recommended to enable testing these observations more quantitatively.

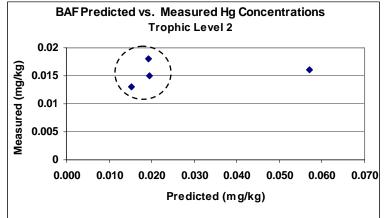
**Table 33**. BAF predicted and measured biota concentrations in Trophic Level 2 Biota

	***		
	Water (mg/L)	Biota (mg/kg)	
Location	DMeHg	Predicted <sup>+</sup>	Measured
Sacramento River (23)*	$9.00 \times 10^{-08}$	0.019	0.018
Napa River (2)	$2.66 \times 10^{-07}$	0.057	0.016
Redwood Creek (9)	$9.09x10^{-08}$	0.020	0.015
Putah Creek (5)	$7.06 \text{x} 10^{-08}$	0.015	0.013
Mokelumne River (0)	$9.62 \times 10^{-08}$	0.021	-
San Joaquin River (0)	$8.06 \times 10^{-08}$	0.017	-
Bear River (0)	$3.51 \times 10^{-07}$	0.076	_
Coyote Creek (0)	$3.07 \times 10^{-07}$	0.066	-
Guadalupe River (0)	$2.54 \times 10^{-06}$	0.546	-
Alamo River (0)	3.78x10 <sup>-06</sup>	0.813	-

<sup>\*</sup> Number of biota samples

Measured water and biota data from the SWRCB database, March 2004.

Figure 7.



Plotted data are from water bodies in Table 33 where data were available for water and biota. Circle indicates predicted BAF values that are closest to their respective measured BAF value.

Table 33 and Figure 7 show that estimates based on the arithmetic BAFs from U.S. EPA data predicted a tissue level similar to the measured biota methylmercury level in three out of the four water bodies selected because data were available for water and biota. The outlying point in Figure 7 is from the Napa River where the water concentration was much higher than the other three rivers, but the biota concentration was similar. The mean values for the three water bodies

<sup>&</sup>lt;sup>+</sup> Calculated from mean measured or converted water concentration (mg/L) x arithmetic mean BAF (2.15E+05 L/kg)

with similar predicted and measured values of methylmercury in biota (excluding the Napa River outlier in Figure 7) were 0.018 and 0.015 ppm, respectively. A two-tailed t-test assuming unequal variance yielded a p = 0.27, thus indicating that these means were not statistically different.

**Table 34**. BAF predicted and measured biota concentrations in Trophic Level 3 biota

	Water (mg/L)	Biota (mg/kg)	
Location	DMeHg	Predicted <sup>+</sup>	Measured
Sacramento River (45)*	$9.00 \times 10^{-08}$	0.119	0.340
Napa River (6)	$2.66 \times 10^{-07}$	0.351	0.260
Redwood Creek (0)	$9.09 \times 10^{-08}$	0.120	-
Putah Creek (10)	$7.06 \times 10^{-08}$	0.093	0.130
Mokelumne River (9)	$9.62 \times 10^{-08}$	0.127	0.310
San Joaquin River (32)	$8.06 \times 10^{-08}$	0.106	0.140
Bear River (2)	$3.51 \times 10^{-07}$	0.463	0.210
Coyote Creek (5)	$3.07 \times 10^{-07}$	0.405	0.140
Guadalupe River (5)	$2.54 \times 10^{-06}$	3.353	0.530
Alamo River (5)	$3.78 \times 10^{-06}$	4.990	0.060

<sup>\*</sup> Number of biota samples

Measured water and biota data from the SWRCB database, March 2004.

BAF Predicted vs. Measured Hg Concentrations **Trophic Level 3** 0.60 Measured (mg/kg) 0.50 0.40 9.30 **d**,20 5.00 10.00 0.00 15.00 Predicted (mg/kg)

Figure 8.

Plotted data are from water bodies in Table 34 where data were available for water and biota. Oval indicates predicted BAF values that are closest to their respective measured BAF value.

<sup>&</sup>lt;sup>+</sup> Calculated from mean measured or converted water concentration (mg/L) x arithmetic mean BAF 1.32E<sup>+06</sup> (L/kg)

Table 34 and Figure 8 show that using the U.S. EPA arithmetic mean BAF for Trophic Level 3 fish predicted the mean mercury tissue level well in seven out of nine cases from the mean concentration of dissolved methylmercury in these water bodies selected because data were available for water and biota. Figure 8 shows two data points that fall outside of the dashed oval. Measured methylmercury in Trophic Level 3 biota was not predicted well for these two water bodies. The Guadalupe River, which is in the highly contaminated New Almaden mercurymining district, had the highest concentration of methylmercury in water and in fish. The Alamo River had a relatively high concentration of methylmercury in water but a very low concentration in fish. This is the only river on this list that is not in northern California, and this river is not known to be associated with potential contamination from mining. In both cases the water concentrations for these outlier water bodies were higher than in the other water bodies, but in one case the predictions were off because the actual biota values were higher (i.e., Guadelupe River), while in the other case they were lower (i.e., Alamo River). These differences might indicate other factors specific to these water bodies are having a large effect on bioaccumulation. The variation in the measured biota data is about four-fold (0.13 to 0.53 mg/kg) compared to the higher variation in the predicted values that range >50-fold (0.09 to 5.0 mg/kg). The mean values for the similar predicted and measured values (excluding the two outlier water body in Figure 9) were 0.24 and 0.22 ppm, respectively. A two-tailed t-test assuming unequal variance yielded a p = 0.79, thus indicating that the means were not statistically different.

**Table 35.** BAF predicted and measured biota concentrations in Trophic Level 4 biota

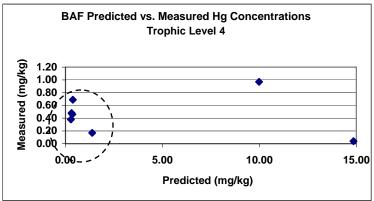
	Water (mg/L)	Biota (mg/kg)	
Location	DMeHg	Predicted <sup>+</sup>	Measured
Sacramento River (125)*	$9.00 \text{x} 10^{-08}$	0.354	0.460
Napa River (0)	$2.66 \times 10^{-07}$	1.045	-
Redwood Creek (0)	$9.09 \times 10^{-08}$	0.357	-
Putah Creek (28)	$7.06 \text{x} 10^{-08}$	0.277	0.380
Mokelumne River (39)	$9.62 \times 10^{-08}$	0.378	0.690
San Joaquin River (261)	$8.06 \times 10^{-08}$	0.317	0.480
Bear River (15)	$3.51 \times 10^{-07}$	1.379	0.170
Coyote Creek (0)	$3.07 \times 10^{-07}$	1.207	-
Guadalupe River (41)	2.54x10 <sup>-06</sup>	9.982	0.970
Alamo River (6)	$3.78 \times 10^{-06}$	14.855	0.040

<sup>\*</sup> Number of biota samples

Measured water and biota data from the SWRCB database, March 2004.

Calculated from mean measured or converted water concentration (mg/L) x arithmetic mean BAF (3.93x10<sup>+06</sup> L/kg)

Figure 9.



Plotted data are from water bodies in Table 35 where data were available for water and biota. Oval indicates predicted BAF values that are closest to their respective measured BAF value.

Table 35 and Figure 9 show that using the U.S. EPA mean BAF for Trophic Level 4 predicts the mean mercury tissue level well in five out of seven cases from the mean concentration of dissolved methylmercury in these water bodies selected because data were available for water and biota. The measured values range about 25-fold (0.04 to 0.97 mg/kg), whereas the predicted values range about 55-fold (0.28 to 14.9 mg/kg). If the low measured value of 0.04 mg/kg is removed from the measured data, then the range is slightly more then five-fold (0.17 to 0.97 mg/kg). This low value was for fish from the Alamo River, which is the only river in this list outside of northern California, an area where mercury from mining is typically a source of mercury in water. As in the case of Trophic Level 3, the two outliers with poor predictability were the Guadalupe and Alamo rivers. These two rivers had higher water concentrations of dissolved methylmercury than others in this list. The mean values (excluding the two outlier water bodies) for the predicted and measured levels of methylmercury in biota were 0.33 and 0.50 ppm, respectively. A two-tailed test with unequal variance for these data yielded a p value of 0.07, not quite significantly different using p < 0.05 as the measure of statistical difference.

### 4.1 OBSERVATIONS CONCERNING THE RESULTS OF TESTING LOTIC BAFS

This exercise shows that the U.S. EPA mean BAFs for Trophic Level 2, 3 and 4 predicted methylmercury tissue values from dissolved water concentrations from California lotic water bodies within qualitative limits in 15 out of 20 simulations, *i.e.*, 75 percent of the time. This is encouraging, but if BAFs are to be used in a regulatory situation it seems prudent to also test them more quantitatively. There are no clear regulatory criteria to use for "predictability," and the database used here is not necessarily complete enough for good statistical testing. One problem with doing this sort of testing is that that it would be necessary to separate natural variation in water and fish concentrations of mercury from lack of predictability. Thus, an additional step for quantifying predictability would be to establish good measurements of natural variation. Some studies have collected potentially useful data for water bodies in California. In five locations in the Sacramento River, Domalgalski (2001) observed an average of 183-fold

fluctuation in the concentration of total methylmercury measured once monthly (dissolved methylmercury is usually about 40-60 percent of total methylmercury, so it is likely that this species would vary about the same amplitude as total methylmercury). Slotton and Ayers (2003), in a study in Cache Creek, reported about four-fold maximum variation in mercury levels in four small forage fish species (red shiners, fathead minnows, green sunfish, mosquito fish) over four seasons. This is less than the observed variation in water concentrations of dissolved methylmercury (greater than biota but less than 10-fold) in Slotton *et al.* (2004). These limited data suggest that natural variability in dissolved methylmercury may be the most important variability to understand and quantify.

A second observation also shows the potential importance of understanding variation in dissolved methylmercury levels. All of the outliers in the qualitative prediction exercise were estimated from water bodies with adequate data for test that had unusually high water concentrations of dissolved methylmercury. At Trophic Level 2, the highest water concentration used in the predictions was for the Napa River. The mean dissolved methylmercury concentration for the four rivers used for prediction was 1.29x10<sup>-7</sup> mg/L and the standard deviation was  $0.92 \times 10^{-7}$ . The water concentration in the Napa River  $(2.66 \times 10^{-7} \text{ mg/L})$  was the only value greater than one standard deviate from the mean. This same pattern is seen for the other trophic levels and water concentrations. For Trophic Level 3, the qualitative outliers for prediction were from the Guadalupe and Alamo Rivers. In this case, the mean dissolved methylmercury concentration for the nine rivers used for prediction was 8.42x10<sup>-7</sup> mg/L and the standard deviation was  $13.54 \times 10^{-7}$ . The water concentrations in the Guadalupe  $(2.54 \times 10^{-6} \text{ mg/L})$ and Alamo Rivers (3.78x10<sup>-6</sup> mg/L) were the only values greater than one standard deviate from the mean. For Trophic Level 4, the qualitative outliers were again from the Guadalupe and Alamo Rivers. In this case, the mean dissolved methylmercury concentration for the seven rivers used for prediction was  $10.01 \times 10^{-7}$  mg/L and the standard deviation was  $15.21 \times 10^{-7}$ . And the water concentrations in the Guadalupe and Alamo Rivers were the only values greater than one standard deviate from the mean. It appears that the BAF concept may not work well for California water bodies with dissolved methylmercury concentrations greater than about 10<sup>-7</sup> mg/L. This should be tested further using more recent data not in the SWRCB database or by collecting new data.

Since the BAF used within a trophic level is the same, the failure in prediction is from applying the BAF to concentrations of dissolved methylmercury that are relatively higher than other water bodies. One standard deviate was a convenient line to use in the current examination, but it might be the wrong criteria to use for the entire distribution of dissolved methylmercury concentrations in lotic water bodies in California. In order to develop a better understanding of factors common to outliers, additional water and tissue data of this type must be subjected to this predictive paradigm and a quantitative criterion to evaluate prediction (*e.g.*, one standard deviate). More needs to be known about the distribution of dissolved methylmercury concentrations in lotic water bodies in California in order to identify important factors effecting water concentrations and bioaccumulation and to determine criteria to test predictions. Similar information should also be gathered about lentic and estuarine water bodies. This information could be used for predictive exercises and possibly to identify and exclude water bodies that are

at the extremes of the distribution of dissolved methylmercury concentrations where default BAFs should not be used because they are not predictive.

One final observation is that the lack of predictability may also be related to situations where extremes of factors that contribute to variation in methylmercury bioaccumulation are at work. The Alamo and the Guadalupe Rivers were identified as outliers in these examples at Trophic Levels 3 and 4. As noted above, the Alamo River was the only river on the list of water bodies used in this exercise that is not in northern California in an area associated with gold or mercury mining. The Alamo River is also in an area impacted by high runoff of salts from agricultural drainage. Both of these factors (salinity/alkalinity or contamination source) are known to effect bioaccumulation, and either could have contributed to the low fish concentrations of methylmercury measured in the Alamo River. On-the-other-hand, the Guadalupe River is in a former mercury mining area and this high contamination could have resulted in unusual conditions in this water body. Identifying extremes of other confounding factors may be important when attempting to test predictability.

### 4.2 CONCLUSIONS CONCERNING THE RESULTS OF TESTING BAF PREDICTIONS

The California SWRCB database contained data for the lotic environment that were useful for testing the accuracy of predicted biota mercury concentrations from dissolved methylmercury water levels through use of arithmetic mean BAFs, which were recalculated from the U.S. EPA BAF data. Due to gaps in available California data for lentic water bodies it was only possible to test BAFs for lentic water bodies. The test dataset contained data from 10 California rivers for which both mercury concentrations in water and biota were compiled in the database. The U.S. EPA translators and BAFs were used to convert water data into tissue concentrations. They qualitatively predicted tissue values in 75 percent of the water body examples for three trophic levels. New water and biota data would be needed to test the California BAFs developed from the SWRCB dataset in the same way. Examination of the results suggests that developing additional quantitative tests would be appropriate since BAFs will be used in a regulatory setting. Examination of the outliers suggests that additional information on natural variation, especially for dissolved methylmercury in California water bodies, is necessary to establish criterion to use to measure predictability and determine when BAFs might not be appropriate. Additional data to determine the distribution of dissolved methylmercury in lentic, lotic and estuarine water bodies in California should be collected. These data could be used to verify whether the default BAF concept works for California water bodies, in particular those with dissolved methylmercury concentrations greater than about 10<sup>-7</sup> mg/L. Data to determine the distribution of mercury in biota in lentic, lotic and estuarine water bodies in California would also be useful in determining how to test and apply default BAFs.

### 5 SUMMARY OF EVALUATION OF BAFs AND TRANSLATORS

OEHHA found that U.S. EPA made a careful effort to compile available data and ensure quality control for the data they used to develop BAFs and translators. Despite their efforts they were not able to compile data representative of all categories of aquatic environments and organisms. In particular their database did not include enough data from which U.S. EPA could develop BAFs for estuarine environments. OEHHA and others noted problems with the U.S. EPA methodology and data. Some of the problems included: the potential for inaccurate identification of biota trophic levels; basing Trophic Level 2 BAFs on organisms that people do not eat; combining data based on different (i.e., not pre-standardized) sampling and measurement techniques; using geometric means without testing the data distributions; low sample size for estuarine translators; and that their database had an uneven geographical and ecological coverage of water bodies. This last point could be especially relevant to California because most of the U.S. EPA data came from the Midwest United States and other areas where the source of mercury in water bodies was atmospheric deposition. California data included by U.S. EPA were from Clear Lake, and some scientific reviewers suggested that these data should be removed because the source of mercury in Clear Lake was different (mercury mining) than for other data. But legacy mining is the predominant source of mercury in many California water bodies, and therefore basing BAFs and translators on conditions associated with this source is important in California. It was also suggested that separate BAFs for a greater number of aquatic environmental categories should be developed and used rather than combining lotic and lentic BAFs into single national default values for each trophic level as U.S. EPA did. OEHHA did find that lotic BAFs were more variable than lentic BAFs and that combining them increased variability. OEHHA also noted that the translator for MeHgt/Hgt was more variable than that for MeHgd/MeHgt, and that directly measuring dissolved methylmercury in water, rather than using translators, helped reduce data variability. But overall OEHHA found that U.S. EPA's methods and results met their goal of developing BAFs and translators that were broadly applicable, especially for lentic and lotic water bodies.

OEHHA reviewed the SWRCB database of mercury measurements in water and biota from California as provided by SWRCB, and examined the BAFs calculated by SAIC. OEHHA found a difference between the way SAIC and U.S. EPA calculated BAFs. In the SWRCB California database measurements of mercury in water and fish were done in different studies and by different researchers. In contrast, mercury in water and biota were measured by the same researchers in the U.S. EPA database. OEHHA grouped measurements on the same water bodies and recalculated BAFs from the SWRCB database in a way analogous to that used by U.S. EPA. OEHHA also calculated translators for some forms of mercury using data available in this database. A number of gaps in available data were identified in the SWRCB database that prevented OEHHA from calculating lentic BAFs and some translators. OEHHA was able to calculate estuarine BAFs for Trophic Level 2 and 4, whereas, U.S. EPA had not calculated BAFs for the estuarine environment. In addition, OEHHA noted that the sample size on which BAFs and translators were based was variable and low in some cases, and that the location of water bodies for which data were available was not evenly distributed throughout the state (i.e., more water bodies were from northern California). OEHHA compared the BAFs calculated from the SWRCB California database for organisms in lotic environments to the U.S. EPA lotic BAFs and demonstrated that they were very similar. The BAF values OEHHA calculated for the estuarine

environment were similar to the national default values, and translators developed from the SWRCB California data were also similar to the U.S. EPA translators. Based on the limited comparisons possible, BAFs and translators based on the California SWRCB dataset and international studies (U.S. EPA database) were found to be similar.

The final step in evaluation of BAFs and translators was to determine how accurately they would predict fish tissue mercury concentrations from water concentrations. U.S. EPA did not test their translators and BAFs. OEHHA was able to test the U.S. EPA national translators and BAFs to see if they accurately predicted mercury levels in fish for several California lotic water bodies by using the SWRCB California database. OEHHA found that the national values predicted California tissue concentrations very well (*i.e.*, no statistical difference between measured and predicted mercury concentration) except for some water bodies where mercury concentrations in water were statistically higher. Mercury concentrations (approximately  $2x10^{-7}$  mg/L or more) in these water bodies were found to be more than one standard deviate from the mean for other data used in these tests. This suggests that translators and BAFs will work well in some lotic water bodies, but not in others, and that it will be important to identify characteristics of water bodies where they work and where they do not. This water value should not be considered a screening level because it has not been tested for enough water bodies. It was not possible to perform similar tests for fish in other types of water bodies due to gaps in the available data for the SWRCB database.

Based on OEHHA's evaluation the national default values for BAFs and translators are well established values that SWRCB can use in an implementation policy for the methylmercury tissue criterion. However, SWRCB should consider OEHHA's finding that these values may not work well for all water bodies in California. With this in mind, OEHHA has identified three alternatives for consideration by SWRCB when selecting BAFs and translators to use to implement the U.S. EPA ambient water quality criterion for methylmercury: 1) use the U.S. EPA BAFs and translators as developed by U.S. EPA for California water bodies; 2) use some BAF (i.e., lotic BAFs) and translator values developed from the California database, and others developed by U.S. EPA; 3) before using BAFs and translators for a methylmercury criterion institute a program of data gathering that would fill in gaps in the California data and enable development and testing of additional BAFs and translators using data from different types of water bodies throughout the state. Alternative 1 is a practical solution that could be implemented without collecting additional data and would be consistent with national implementation. Based on OEHHA's evaluation using available data it will also yield predictions that are similar to measured concentrations of mercury in fish for many but not all lotic water bodies. It is unknown how well this alternative will work for other California water bodies. Alternative 2 is appealing because it would incorporate California data and values for lotic water bodies, but due to data gaps it would also require using national values for lentic water bodies and some translators. However, since OEHHA's evaluation found no significant difference between U.S. EPA and California values based on the existing database there is no scientific basis to support this alternative over Alternative 1. Alternative 3 would require collecting additional data on mercury concentrations in water and biota before full implementation and should include establishing standards for sampling, analytical methods, and Quality Assurance/Quality Control before data collection begins. Additional data collection is important to consider because

OEHHA was not able to test Alternative 1 for California lentic and estuarine water bodies using the current datasets and because some water bodies were identified where Alternative 1 did not work well.

OEHHA recommends that SWRCB consider collecting additional data representing a wide variety of water bodies spread throughout the state where BAFs and translators will be used as part of regulatory implementation for the methylmercury criterion. Alternative 1 could be used on a short term basis and collecting additional data could be used on a longer term basis to improve BAFs and translators used in California. Additional data for mercury concentrations in fish and water could fill data gaps, help identify biogeochemical factors with the greatest impact on methylmercury production and bioaccumulation, and better characterize how these affect variability in BAFs and translators. With enough good data it should be possible to identify water body types or geographic regions where national or California default BAFs and translators are more or less accurate. This would be a continual test of the BAF concept and default values. The results could be used to further test and verify the U.S. EPA or California values, or lead to developing better options, or options for water body types where the current values work poorly. SWRCB should consider prioritizing data collection based on which type(s) of water bodies are most impacted by regulatory implementation.

In particular more fish and water data are needed for: 1) lentic BAFs and translators; 2) to fill in data gaps for estuarine translators and Trophic Level 3 biota; and 3) to collect enough data to test lentic and estuarine BAFs and translators. Standard collection and analysis methods for mercury in water should be established as part of a program to collect more data. Measuring dissolved methylmercury directly should be considered as part of this program to reduce the variability that occurs when converting between mercury forms in water. It would be useful to also measure other forms of mercury in water (*e.g.*, total physical and chemical mercury, dissolved total mercury, etc.) to develop and test translators that might still be needed in some cases.

Collecting additional California data is also recommended to better characterize variability in mercury concentration in California water bodies and biota. Natural variability in mercury concentrations will occur in water and fish from any water body. Statistical tests such as those used by OEHHA to test BAF predictions account for variability when testing for true differences. But statistical testing is not typically used in regulatory applications and permits. One way to recognize variability in a regulatory setting would be to collect more data to separate variability due to environmental differences from variability common to all environments and use this to verify predictions and set regulatory limits.

Further data and testing would put BAFs and translators on a more sound scientific footing in California and provide data to determine whether the mining source of much of the mercury in California water bodies (at least in the Central Valley, northern California, and the Coast Ranges) lead to significant differences in BAFs and translators for some parts of the state.

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#### **GLOSSARY OF TERMS**

- **arithmetic mean (AM):** is a measure of central tendency for the values in a distribution. It is commonly called the average, and is calculated by summing the data values and dividing the sum by the total number of data values.
- **BAF** (Converted): Converted BAFs are derived from studies where the concentration of the measured mercury form in the water must be converted to dissolved methylmercury in order to calculate a BAF.
- **BAF** (**Direct**): Direct BAFs are derived from studies where the concentration of dissolved methylmercury was measured and therefore can be used directly in the calculation a BAF.
- **bioaccumulation:** The accumulation of chemicals in living organisms through the food web, *i.e.*, the accumulation of chemicals from one organism into another after it is eaten. When chemical metabolism and elimination of a chemical are slow chemicals may biomagnify through the food web. In this case the concentration increases with every step in the food web.
- **bioaccumulation factor** (**BAF**): A bioaccumulation factor is the ratio between the concentration of a chemical measured in an organism and the concentration of the same chemical in water. This ratio is derived from field-collected samples of organisms and water.
- biota: the living organisms (plant and animal life) in an area or ecosystem.
- estuarine environment: The aquatic environment formed where freshwater from an inland river meets and mixes with saltwater from the ocean. Organisms in this environment are usually adapted to the different environmental conditions that occur where there is a mixture of fresh and saltwater. An example in California is the San Francisco Bay estuary that lies between the Pacific Ocean and the Sacramento and San Joaquin rivers.
- **geometric mean (GM):** A geometric mean is used as a central tendency estimate for data that are log-normally distributed. The geometric mean is calculated by converting all data values to a log<sub>10</sub> value, then the arithmetic mean of these transformed values is calculated. Finally the antilog of the arithmetic mean is calculated which is then geometric mean. Geometric means are used as estimates of central tendencies to reduce the influence of high values in the distribution.
- **lentic environment**: An aquatic environment characterized by still (not flowing) water, *e.g.*, lakes and reservoirs.
- **log-normal data distribution:** A distribution of values that is normally distributed when the raw values are transformed by taking the natural logarithm of each value. The values in log-normal distributions may range over several orders of magnitude, 1-100, 1,000, 10,000.

- **lotic environment:** An aquatic environment characterized by flowing water, *e.g.*, streams and rivers.
- **mercury: dissolved:** Dissolved mercury is any chemical form of mercury (inorganic or organic) measured in the water that passes through a small pore (micron) filter.
- mercury: total: Total mercury is the sum of the concentrations of all chemical and physical forms of mercury in some medium. In fish tissue total mercury is the sum of inorganic and organic (methyl) mercury. In water it is the sum of all dissolved chemical and physical forms that are measured in water that flows through a filter plus the concentrations of the same forms retained on the filter. So total mercury might, in some cases, refer to the dissolved inorganic mercury plus inorganic mercury that is retained on the micron filter. The text specifies whether this term refers to all chemical and physical forms or some subset.
- **methylmercury: dissolved:** Dissolved methylmercury is measured as the concentration of methylmercury from that passes through a micron filter. It is the form that is used in BAF calculation because it is considered the form that is most easily accumulated from water by biota, and the form which of greatest human health concern.
- **methylmercury: total:** Total methylmercury is the sum of dissolved methylmercury that passes through a micron filter and the concentration of methylmercury mercury that is retained on a micron filter.
- micron filter: Filters with small pore (hole) sizes. Micron filters used for characterizing of the forms (dissolved and non-dissolved) of mercury in water have diameters in the range 0.2-0.8 μm (2E-07 to 8E-07 meter) range.
- **microseston**: The total suspended microscopic organic and inorganic matter in an aquatic environment.
- **phytoplankton**: The portion of the plankton community comprised of living tiny plants (*e.g.* algae, diatoms) that are primary producers of energy.
- **p-value** (**statistic**): The probability of a Type I error (*i.e.*, rejecting a true null hypothesis) occurring based on a statistical test. Typically a p-value of 0.05 (5% significance level) or below is used as the smallest level of significance to declare that there is a true difference between two data sets being compared (*e.g.*, finding that the arithmetic mean values for two data sets are different). Lower and higher p-values can be used. A p-value of p  $\leq$ 0.05 (5% significance) has been used in the report.
- **SAIC**: Science Applications International Corporation. This organization compiled a database of California mercury measurements in water and biota.
- **SWRCB**: State Water Resources Control Board.

**Translators:** Empirically derived factors (ratios) used for the conversion between forms of mercury. In this case, the translators are for different forms of mercury in water and are based on field-collected samples that occur in water into forms that can be used in the regulatory process. The U.S. EPA derived translators for the relationships of dissolved inorganic mercury to total inorganic mercury, dissolved methylmercury to total inorganic mercury and dissolved methylmercury to total methylmercury.

**trophic level:** Trophic means eating. Trophic levels are steps in a food chain characterized by feeding interactions. Energy moves up the food chain from lower to higher trophic levels as a result of organisms in one level feeding on those in a lower level. Organisms in Trophic Level 1 are primary producers that fix energy in an ecosystem (*e.g.*, plants and other organisms that fix energy. Trophic Level 2 organisms are herbivorous and feed on the primary producers. In aquatic ecosystems Trophic Level 3 organisms eat the herbivores and are forage fish for the next level. Trophic Level 4 organisms are carnivorous and eat primarily Trophic Level 3 organisms. In aquatic ecosystems these are the top predatory fish. Humans mostly eat fish and other aquatic organisms from Trophic Level 3 and 4.

**zooplankton**: Small (often microscopic) free-floating aquatic animals near the base of the food web (*i.e.* primary consumers).

# APPENDIX 1: Criteria for Including Data in the California MeHg Database\*

- 1. Data should be a primary source (provided by the funding organization or data collectors). It should not be from a database such as STORET where there are multiple sources combined, unless the source of the data is clearly identified.
- 2. The methods used (including sample preservation, sample handling, and analytical method) should be ascertainable. Note that sometimes the analytical method defines sample preservation and handling, so analytical method may sometimes be sufficient.
- 3. The units of all observations must be clearly identified.
- 4. Sampling dates year should be specified at a minimum (day, month, and year are preferred)
- 5. Location of samples should be identified, including water depth, if appropriate. Location of samples should be by lat long, or other unique coordinates that locate the sample within a waterbody, not just in a waterbody or waterbody segment. May also use location naming information such as Sac River at river mile 44 or if map is available with station locations.
- 6. Fish Tissue Sample Type sample must be filet either with or without skin (whole fish is not acceptable).
- 7. Fish Species The common name or species name of the fish sampled must be apparent so that the trophic level can be determined.
- 8. Any notes on individual samples should be interpretable. We need to know what a "j," "k," or "l" means, and what samples were nondetects.
- 9. The analytical laboratory should be identifiable. The objective here is to ensure that data are professionally analyzed.
- 10. The sampling organization should be identifiable if different from the analytical laboratory. Particularly with Method 1631, sampling is complicated and should be done by fully trained and qualified staff.
- \*(personal communication from Diane Fleck, U.S. EPA, Region 9)